



Practical and Analytical Chemistry: A Complete Course in Chemical Analysis

Henry Trimble

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Henry Trimble



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PRACTICAL AND ANALYTICAL

CHEMISTRY.

A COMPLETE COURSE IN CHEMICAL
ANALYSIS.

BY

HENRY TRIMBLE, Ph.M.,

PROFESSOR OF ANALYTICAL CHEMISTRY IN THE PHILADELPHIA COLLEGE
OF PHARMACY.

FOURTH EDITION.

WITH ILLUSTRATIONS.

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1892.

Preface to the Fourth Edition.

In the preparation of this edition the author has made such additions and changes as, in his experience with the use of the book in large classes, he has found to be desirable.

Slight additions have been made to the charts for the separation of bases, wherever it has been found that fuller explanations were needed. It is very important, however, that the student should not be allowed to become too mechanical in this part of the work, and thereby overlook the reasons for carrying out the processes as described. This difficulty may be obviated by the teacher frequently questioning the student, and in large classes delivering short lectures in which the separations are explained and the reactions involved written out, so as to emphasize the fact that every step in an analytical operation is strictly a chemical process.

The use of formulas and symbols for the reagents, instead of the full chemical name, has been continued in this edition. They may be inconvenient at first, but the student soon learns them, almost without effort, and thus becomes familiar with what he should know, but should not be compelled to memorize.

H. T.

January, 1892.

Preface to the First Edition.

The increased amount of time devoted by students of pharmacy and medicine to analytical chemistry has directed more attention to the subject of imparting instruction in this science.

The object of the present volume is to place before the student as compact a course as possible, in order to enable him to become familiar with the subject in the necessarily limited time at his disposal.

The author's experience has led him to believe that a study of Qualitative Analysis should be preceded by some experience in the preparation of the more important gases and a few of the salts. Such practice requires the student to familiarize himself with the construction of apparatus as well as with the processes of filtration, evaporation, crystallization, ignition, etc.

The examples for preparation may be increased at the option of the instructor.

In Part II the student should perform the reactions of each group, and then be furnished with a solution containing some, or all, of the bases of the group. This should be followed by a solution in which he should search for all the elements previously studied; such practice being repeated until he can correctly determine all the bases present.

In order to enable the student to see the comparative effect of the group reagents readily, a summary has been introduced at the end of each group. This he should be able to write out, without the use of the book, before attempting to analyze a group solution. By progressive steps he is thus led rapidly on to successfully examine the more complex solutions for both bases and acids.

The grouping of the bases is, to a certain extent, new, but it places together those elements which are very closely related, and, in addition, adapts each group to the time of one lesson ; which may be repeated if desirable.

In the Part devoted to the gravimetric and volumetric analysis, the examples are limited in number ; but this much is intended to give the student an opportunity to learn the methods with the aid of an instructor, so that he may afterward pursue the subject alone, with the aid of a book like Fresenius's "Quantitative Analysis."

In conclusion, it is but just to state that many of the works on Qualitative Analysis have been consulted.

Those of Attfield and Mütter furnished many valuable hints, but Fresenius's admirable work has been used as authority, and, to those who wish to pursue the subject in greater detail than here offered, it is recommended for reference.

H. T.

Philadelphia, August 19th, 1885.

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PART FIRST.

PRACTICAL.

PRACTICAL AND ANALYTICAL CHEMISTRY.

PART I.—PRACTICAL.

SECTION I.

PREPARATION AND PROPERTIES OF SOME NON-METALS AND THEIR COMPOUNDS.

HYDROGEN, H.

Preparation.—Place a few fragments of zinc in a flat-bottom flask of about one-fourth liter capacity; cover the zinc with water and adapt a cork, through which pass two tubes (Fig. 1), one just reaching through the cork and bent so the long end may be dipped under water, the other running directly from a short distance above the cork nearly to the bottom of the flask, so as to be below the surface of the liquid. The upper end of this tube should have a small funnel placed in it, or be enlarged by softening in the flame, inserting and revolving a file or similar instrument, previously warmed.

Add, slowly, a small quantity of sulphuric acid, through this tube, and notice an immediate effervescence, with the escape of bubbles through the water in which the exit tube dips. Fill a test tube with water, and, keeping the open end under the liquid, bring it over the tube, so as to collect the gas. When full, close with the thumb, and, bringing the mouth of the tube near a flame, quickly remove the thumb and allow the gas to ignite. It will burn quietly if the gas be pure, but with a slight explosion if it be mixed with air.

Properties.—This gas is **Hydrogen**, and its physical properties may now be studied by observing that it is insoluble in water, and without odor, color or taste.

EXPERIMENT I. Collect a tube full, and holding it, covered, in a vertical position, bring a lighted taper a short distance above its mouth and remove the cover; the gas will ignite, showing its great levity.

EXPERIMENT II. Another tube, similarly filled, is held in an inverted position, and the cover removed; it will be found,

FIG. 1.



even after the lapse of some time, that the hydrogen at the mouth of the tube may be ignited, thus demonstrating that the gas is too light to come down and out the mouth of the tube. These two experiments have also demonstrated the combustibility of the gas, which, when pure, burns quietly, with a colorless flame. If, however, it be mixed with air and flame applied, a violent explosion ensues. *Therefore, the tube from the generator should never be brought near a flame until it is certain all the air has been expelled.* This is determined by

trying a test tube full ; if it burn quietly, the jet may be lighted. *This precaution should always be observed.*

EXPERIMENT III. On bringing a lighted taper to the mouth of a tube full of hydrogen, the gas is ignited, but on pushing the burning taper up into the gas its flame is extinguished, thus showing that while hydrogen is combustible it is not a supporter of combustion.

EXPERIMENT IV. Continue the addition of acid to the zinc until the latter is nearly all dissolved ; disconnect the apparatus, pour the liquid on a filter, collect the filtrate in a small beaker or evaporating dish, concentrate and set aside for twenty-four hours, to crystallize. These crystals are *zinc sulphate*, ZnSO_4 , the result of a combination of the sulphuric acid and the zinc, as follows :—



CHLORINE, Cl.

Preparation.—In a flask, arranged so that heat may be applied (Fig. 2), place a small quantity of manganese dioxide, add hydrochloric acid, agitate well, to moisten all the powder on the bottom, and apply heat. A yellowish-green gas is evolved, which, being somewhat soluble in water, may be collected by *downward displacement*, that is, by running the delivery tube to the bottom of the receptacle, loosely covered ; the heavy gas displaces the lighter air.

If the evolution be moderately active it may be collected over warm water, as only a small loss occurs. Care should be taken to avoid inhaling the gas, by passing it, when not collecting, into a solution of potassium or sodium hydrate. The following expresses the reaction in symbols :—



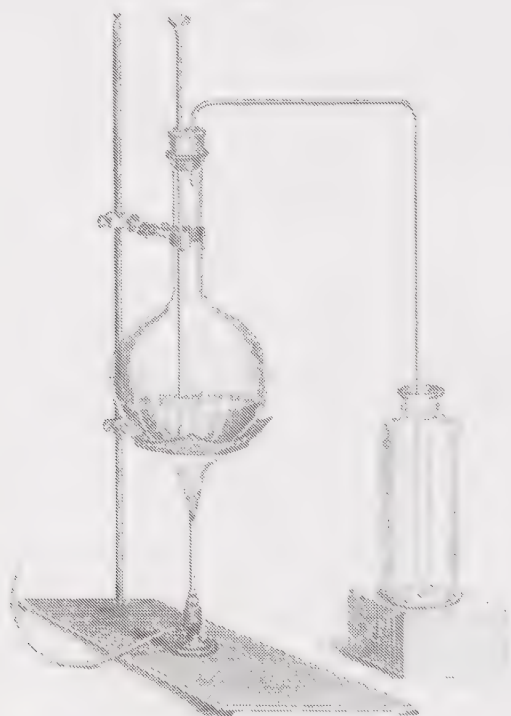
Properties.—EXPERIMENT I. Pass the gas into water ; it is absorbed ; if this be continued until the water is saturated, it will be found to have absorbed about twice its volume of the gas ; the *Aqua Chlori* of the Pharmacopœia is the resulting product.

EXPERIMENT II. A tube full of the gas held with mouth upward, and a lighted taper applied, fails to ignite. Push the

taper into the gas; it is extinguished, or only burns with a small, dense, smoky flame, the result of a combination of the chlorine with the hydrogen of the wax, liberating the carbon.

EXPERIMENT III. Into a tube full of the gas put a piece of brightly dyed calico or blue litmus paper, previously moistened; it is rapidly bleached. Writing on paper is simi-

FIG. 2.



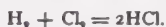
larly decolorized, but printing is not affected, as it contains carbon, in the form of lampblack, which is not acted on by the gas. If the experiments be made with chlorine which has been passed through sulphuric acid to dry it, and the materials are not moistened, no decoloration takes place.

The process of bleaching by chlorine is one of *oxidation*; it

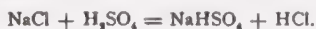
combines with the hydrogen of the water, forming hydrochloric acid, while the liberated oxygen in the nascent state readily attacks the coloring matter, water and a colorless compound resulting.

HYDROCHLORIC ACID, HCl.

Preparation.—Collect one test tube full of hydrogen and one of chlorine, bring their mouths together (the hydrogen tube above with mouth down, as it is lighter), turn over once or twice, so as to thoroughly mix, and open their mouths to a flame; a sharp report will occur, with the development of strongly acid fumes, which will be recognized by future tests as *hydrochloric acid* :—



To prepare a quantity of it, the apparatus used for the preparation of chlorine serves best. Put into the flask some sodium chloride (common salt), add sulphuric acid slowly, and when the evolution of gas ceases apply a gentle heat. Collect by downward displacement or over mercury :—



The above expresses the reaction when an excess of acid has been used, which is preferable, as the resulting acid sodium sulphate is easily dissolved out of the flask with water. On the large scale the following more economical method is used :—



Properties.—The pungent, suffocating odor and freedom from color are noted with its production.

EXPERIMENT I. A test tube or jar of the gas placed with the open mouth under water will so rapidly dissolve that the liquid rises in the vessel. This solution of the gas in water, when of the proper strength, is the *Acidum Hydrochloricum*, U. S. P.

EXPERIMENT II. A piece of moistened blue litmus paper held in a tube of the gas is instantly reddened.

EXPERIMENT III. A lighted taper applied to the gas fails to ignite it, and is extinguished if lowered into it.

EXPERIMENT IV. Bring a rod moistened with ammonia over the mouth of a tube full of the gas: dense white fumes of ammonium chloride are formed.

The mixture remaining in the flask dissolved in warm water, treated with sodium carbonate so long as effervescence occurs, to neutralize the excess of sulphuric acid, concentrated, filtered and set aside to crystallize, yields *sodium sulphate* (Glauber salt).

BROMINE, Br.

Preparation.—Pass chlorine into a one per cent. solution of potassium bromide. The liquid will become reddish-brown in color, owing to separation of bromine which remains dissolved in the water.

EXPERIMENT I. To a portion of this solution add a solution of starch; a yellow color will be developed, due to the formation of a compound of starch with bromine.

EXPERIMENT II. To the remainder of the solution in a test tube add a small quantity of chloroform and agitate. The chloroform will remove the bromine from the water and will settle to the bottom of the tube as a deep reddish-brown liquid, while the water above will become nearly colorless.

IODINE, I.

Preparation.—Pass chlorine into a one per cent. solution of potassium iodide. The liquid will become dark in color, owing to separation of iodine. Stronger solutions would result in the precipitation of the iodine.

EXPERIMENT I. To a portion of the iodine solution, diluted with water, add solution of starch; a blue color will form, due to the combination of starch with iodine. When a precipitate is formed instead of a blue color it is an indication that the iodine solution is too strong, and a more dilute one of the iodine must be used. The blue color of the starch iodide is destroyed by heat and by an excess of chlorine.

EXPERIMENT II. To another portion of the iodine solution in a test tube add a small quantity of chloroform and agitate.

The chloroform will remove the iodine from the water and settle to the bottom of the tube as a deep violet-colored liquid, and the water above will become colorless.

OXYGEN, O.

Preparation.—Place a few crystals of potassium chlorate in a clean and dry test tube, adapt a delivery tube long enough to reach under the surface of some water near by. Apply a steady flame, taking care not to allow any water to be drawn back into the tube; as soon as the bubbles of gas escape freely and the air has been expelled, bring a test tube filled with water over the escaping gas, and collect it. It is **Oxygen**, produced from the potassium chlorate by heat, according to the following reaction:—



Properties.—The appearance and insolubility of the gas in water are noted as it is collected.

EXPERIMENT I. The gas is not ignited by the application of a lighted taper. The taper, however, will burn with greatly-increased energy if it be plunged into the gas. If the flame be extinguished and the taper again brought into the gas, provided a spark remain, the taper will be rekindled.

EXPERIMENT II. A piece of charcoal, previously ignited, is lowered into the gas; a rapid combustion ensues, and the charcoal disappears. Pour some lime water into the tube, agitate well; a white precipitate of calcium carbonate is produced. If this be tried with oxygen previous to the burning of the charcoal, no precipitate will be formed. A number of other substances, as sulphur, phosphorus, and even iron, when once kindled, will burn in oxygen with great brilliancy, forming characteristic oxides.

EXPERIMENT III. Take two test tubes, one about twice the capacity of the other. Fill the larger with hydrogen and the smaller with oxygen, bring their mouths together, and, after turning once or twice, to thoroughly mix their contents, open them and apply flame. A sharp report is caused by the combination to form water.

If more than two volumes of hydrogen to one of oxygen be present, the surplus remains uncombined; if oxygen be present in greater proportion, the excess of it remains.

SULPHUROUS OXIDE, SO_2 .

Preparation.—In a flask, arranged as for the preparation of chlorine, place a few copper turnings and cover them with concentrated sulphuric acid. Apply a gentle heat, gradually increasing until effervescence commences, and collect the resulting gas by downward displacement, as in the case of chlorine. This gas is sulphurous oxide, and its formation takes place according to the following equation:—



Properties.—As will be noticed during its collection, this is a colorless, heavy gas, of a suffocating odor.

EXPERIMENT I. A tube full of the gas inverted in a vessel of water will show the ready solubility of it in that liquid.

EXPERIMENT II. A piece of moistened blue litmus paper held in a tube of the gas will momentarily become red and then white, thus showing its active bleaching property.

EXPERIMENT III. A lighted taper plunged into a tube full of the gas is quickly extinguished, indicating that it is neither combustible nor a supporter of combustion.

EXPERIMENT IV. Pass the gas into water until the latter smells strongly of it, then add to the resulting solution a solution of potassium permanganate. The purple color of the latter will be destroyed as rapidly as added.

Sulphurous oxide is an active reducing agent, that is, it combines with the oxygen of other compounds. In this respect its action is directly opposite to that of chlorine.

NITROGEN, N.

Preparation.—The usual method of preparing this gas is to deprive air of its oxygen, leaving the nitrogen pure. This is best accomplished by placing a small fragment of phosphorus on a cork covered with some fireproof material. Float

the cork and phosphorus on water, ignite the latter and bring over it a bell-jar. The phosphorus combines with the oxygen, converting it into phosphorus pentoxide, P_2O_5 , which dissolves in the water present, thus leaving the nitrogen pure. A better method for obtaining larger quantities is to heat a mixture of potassium nitrite and ammonium chloride dissolved in water. When the reaction begins, the temperature must be carefully watched, in order to prevent the too rapid evolution of the gas:—



Properties.—The physical properties have been observed during its preparation and collection. In regard to chemical properties, it is inert in the free state. Its compounds, however, are very energetic.

AMMONIA, NH_3 .

Preparation.—In a test tube or evaporating dish mix equal quantities of powdered calcium oxide (quicklime) and ammonium chloride, with a few drops of water; the odor of ammonia will be immediately developed:—



In smaller quantities the gas may be recognized by holding over the mixture a strip of moistened red litmus paper; it will slowly become blue; or similarly hold a glass rod moistened with hydrochloric acid; dense white fumes of ammonium chloride will form. To prepare larger quantities of the gas, heat the ordinary water of ammonia, which, at a comparatively low temperature, gives it off freely. If it be desired to dry the gas, it must be passed over quicklime. Ammonia is collected by *upward displacement*, that is, by passing the delivery tube upward into a jar or test tube inverted over it; being lighter than air the latter is displaced.

Properties.—EXPERIMENT I. Place a vessel filled with ammonia gas, mouth downward, into some water, and agitate slightly; the water will rise in the vessel rapidly, nearly filling it, showing the great solubility of the gas in water. The other physical properties, as color, odor, etc., have been noted during its collection.

EXPERIMENT II. On applying a lighted taper to the gas it does not burn; if, however, it be mixed with oxygen it will ignite readily. On introducing the taper into the gas it is extinguished.

NITRIC ACID, HNO_3 .

Preparation.—Place a small quantity of potassium nitrate in a test tube, and cover it with strong sulphuric acid. Apply a gentle heat; brown, strongly acid fumes are given off. Dilute with a little water and add indigo solution; it is decolorized. This is a characteristic test for nitric acid.

To prepare a larger quantity a retort is used, to which is adapted a glass receiver. The nitric acid distills over on the application of a moderate heat, forming a reddish-yellow liquid, which rapidly attacks and destroys organic matter.

Two reactions may be employed to represent the production of nitric acid, depending on the relative quantity of the materials used. In the first case an excess of sulphuric acid gives—



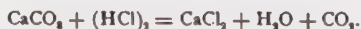
In the second case just a sufficient amount of sulphuric acid is used to decompose the potassium nitrate—



On the large scale sodium nitrate is now employed in place of the potassium salt, on account of its lower price.

CARBON DIOXIDE, CO_2 .

Preparation.—The flask used in the preparation of hydrogen will serve for making carbon dioxide. A few pieces of marble are placed in the flask, covered with water, and hydrochloric acid added. A brisk effervescence ensues, and the gas being somewhat soluble in water is collected by downward displacement:—



Sulphuric acid should not be used, as it forms an insoluble calcium sulphate which is very difficult to remove from the flask.

Properties.—**EXPERIMENT I.** Pour some clear lime water into a jar of the gas and agitate; the solution immediately becomes cloudy, owing to formation of insoluble calcium carbonate. If more gas be passed into the mixture it will become nearly clear again, on account of the solubility of the precipitate in carbonic acid.

EXPERIMENT II. Add solution of potassium hydrate to a jar of the gas, close and shake well; the gas is absorbed by the alkali, as may be shown by placing the mouth of the jar under water and removing the stopper, when the water will rush in, nearly filling it.

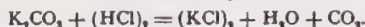
EXPERIMENT III. A lighted taper lowered into the gas is immediately extinguished. The same result is accomplished by opening the vessel some distance above the flame and allowing the gas to flow down upon it. This latter experiment also illustrates the great density of the gas, which is twenty-two times heavier than hydrogen.

SECTION II.

PREPARATION OF SALTS.

POTASSIUM CHLORIDE, KCl.

Preparation.—One or two cubic centimeters of hydrochloric acid, diluted with three or four times its bulk of water, are placed in a small beaker glass, and potassium carbonate added so long as effervescence occurs, and until after boiling (to remove CO_2) the solution is neutral to litmus paper, that is, when the blue litmus paper is not changed to red nor the red changed to blue. Filter, evaporate to a small bulk and set aside to crystallize. The cubic crystals which separate after standing twenty-four hours may be collected on filter paper and dried at a moderate temperature:—



Potassium chloride is rarely prepared in this manner, except for practice, as it occurs largely in nature, and is used for preparing many other potassium salts.

POTASSIUM AND SODIUM TARTRATE,



(ROCHELLE SALT.)

Preparation.—Heat, in a porcelain capsule, a solution of sodium carbonate, and add to it potassium bitartrate until effervescence ceases, and the solution (after the escape of CO_2) is neutral to litmus. On filtering and cooling, crystals of Rochelle salt are deposited, rapidly and in small crystals if the solution be concentrated, but slowly and in much larger ones if the solution be dilute:—



Note on Calculation —In order to calculate the amount of each salt to use in the above process, we notice the number of molecules of each employed, and multiply this by the sum of the atomic weights (that is, by the molecular weights). In the above case one molecule of $\text{Na}_2\text{CO}_3 = 106$, and two molecules of $\text{KHC}_4\text{H}_4\text{O}_6 = 2 \times 188.1 = 376.2$. Therefore every 106 parts of anhydrous sodium carbonate require 376.2 parts of potassium bitartrate, to form Rochelle salt. If we have 50 grams of anhydrous sodium carbonate and wish to convert it into Rochelle salt, we use the following formula: As 106 : 376.2 :: 50 grams : number of grams of potassium bitartrate required, = 177.4 grams.

AMMONIUM NITRATE, NH_4NO_3 .

Preparation.—Add to about 20 c.c. of dilute nitric acid, in a beaker glass, sufficient ammonia water to give it a distinct ammoniacal odor; filter, concentrate, keeping the ammonia in slight excess, and set aside in a cool place for crystals to form:—



Properties.—These crystals contain twelve molecules of water of crystallization, which it is desirable to get rid of before using the salt. By exposure to a temperature of 155°C . the water gradually escapes, and the fused or granulated salt is ready to be converted into nitrogen monoxide (laughing gas), which takes place at about 185°C . according to the following reaction:—

AMMONIUM OXALATE, $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

Preparation.—Dilute 20 c.c. of solution of ammonia with twice its bulk of water, add a solution of oxalic acid until neutral, concentrate slightly, filter and set aside to crystallize. The crystals may be collected on a filter, and another crop obtained by concentrating the "mother liquor":—



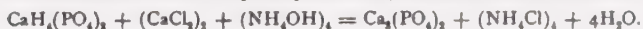
Ammonium carbonate is sometimes used for combining with the oxalic acid, but the neutralization is not as easily effected, besides it is not desirable on the ground of economy.

CALCIUM PHOSPHATE, $\text{Ca}_3(\text{PO}_4)_2$.

Preparation.—Finely powdered bone ash is digested for a short time with diluted hydrochloric acid. The solution is filtered, boiled, and filtered again, if necessary. The filtrate is treated with ammonia until it smells strongly of it. Collect the precipitate on a filter, wash by pouring on warm water until the washings are tasteless, and dry at a low temperature. The resulting powder is calcium phosphate, which exists in the bone ash and is dissolved by hydrochloric acid, forming acid calcium phosphate, as follows:—



From this solution it is precipitated by ammonia, as follows:—



In addition to the ordinary apparatus with which a student supplies himself, there is required a *wash bottle* (Fig. 3), which it is well for every student to construct for himself, as it furnishes him valuable practice in cutting and bending glass tubing. This bottle is used in washing all precipitates, and is convenient as a water supply, which may be kept hot, if desired.

MAGNESIUM SULPHATE, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Preparation.—To about 5 c.c. of dilute sulphuric acid, diluted with five or six times its volume of water, heated in a

FIG. 3.

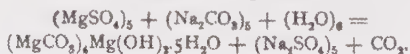


capsule, add powdered magnesium carbonate until effervescence ceases, and filter. Concentrate and set aside to crystallize.



MAGNESIUM CARBONATE, $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

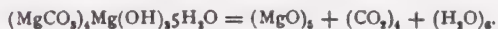
Preparation.—On mixing solutions of magnesium sulphate and sodium carbonate and boiling, we get magnesium carbonate precipitated, while carbon dioxide escapes. The precipitate is very variable in its composition, depending on the concentration of the solutions. When the U. S. P. product is obtained the following equation expresses the reaction:—



The precipitate washed with hot water and dried, serves for the following example of a compound prepared by *ignition*.

MAGNESIUM OXIDE, MgO .

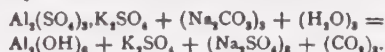
Preparation.—Heat some of the magnesium carbonate, prepared in the above reaction, in a porcelain crucible until, on taking out a small portion, placing in a test tube with a little water, heating to remove air bubbles, and adding a drop or two of hydrochloric acid, no effervescence is produced. This will require some time, and great care is necessary to determine when the powder fails to give an effervescence with the acid.



Zinc oxide may be prepared in a similar manner, from zinc carbonate. This differs from the magnesium oxide by being yellow while hot, and very pale yellow when cold.

ALUMINIUM HYDRATE, $\text{Al}_2(\text{OH})_6$.

Preparation.—To a solution of alum add a solution of sodium carbonate and boil. Allow the precipitate to settle, decant the clear supernatant liquid on a filter, add more hot water to the precipitate and again decant. Collect the precipitate on the filter, wash well with hot water and dry; the resulting white powder is *Aluminii Hydras*, U. S. P.



FERROUS SULPHATE, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Preparation.—Add enough dilute sulphuric acid mixed with ten volumes of water to some iron filings, or wire, in a beaker, to more than cover them. Allow the reaction to proceed, assisted by a little heat, until effervescence ceases. Filter from the excess of iron, concentrate, filter and crystallize.



These crystals should be rapidly dried and preserved in well-stopped bottles, as they quickly become converted into ferric sulphate on exposure to air.

FERRIC SULPHATE, $\text{Fe}_2(\text{SO}_4)_3$.

Preparation.—To a strong solution of ferrous sulphate add one-fourth its bulk of sulphuric acid, heat to the boiling point and drop in nitric acid as long as effervescence is produced

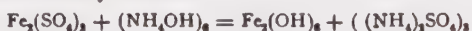
and until the resulting liquid becomes of a clear reddish-brown color.



This is the *Liquor Ferri Tersulphatis* of the Pharmacopœia; and is the most convenient compound to use in the preparation of some of the other iron salts.

FERRIC HYDRATE, $\text{Fe}_2(\text{OH})_6$.

Preparation.—Dilute some of the above ferric sulphate solution with an equal bulk of water, add solution of ammonia until, after stirring, it smells strongly. The resulting precipitate is *ferric hydrate*, the well-known antidote to arsenic. When needed for this purpose, it is sufficient to pour the mixture on a muslin strainer, wash once or twice until the saline taste nearly disappears from the washings, when the compound is ready for use.



This preparation should always be freshly prepared when wanted for use as an antidote, as it loses H_2O on keeping, becoming a mixture of ferric oxide Fe_2O_3 and hydrate. This change takes place, although more slowly, when the compound is kept under water.

COPPER SULPHATE, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Preparation.—Heat copper turnings for some time, with strong sulphuric acid, in a fume closet, until the reaction ceases. Dilute with water, filter and crystallize.



LEAD ACETATE, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$.

Preparation.—Lead oxide (litharge) is boiled with three or four times its weight of acetic acid, in a capsule, adding water from time to time, with more acid, if necessary, until most of the oxide has disappeared. Filter, concentrate, keeping the solution acid, and set aside to crystallize:—



The solution or crystals should not be exposed to the fumes of the laboratory, for if there be only a small quantity of hydrogen sulphide in the room, they will become black.

PART SECOND.

QUALITATIVE ANALYSIS.

PART II.—QUALITATIVE ANALYSIS.

SECTION I.

BASES.

GROUP I.—POTASSIUM, SODIUM, LITHIUM, AMMONIUM.

REACTIONS OF POTASSIUM (K).

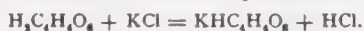
Use a solution of potassium chloride (KCl).

1. PtCl_4 added to some of the above solution of KCl, causes a yellow crystalline precipitate of K_2PtCl_6 , soluble in excess of water.



The delicacy of this reaction is increased by the addition of alcohol. This precipitate should be preserved to compare with a similar one under ammonium.

2. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, in concentrated solution, added to another portion of the KCl, produces a white crystalline precipitate of **acid potassium tartrate**— $\text{KHC}_4\text{H}_4\text{O}_6$, soluble in excess of water, readily in hot water, acids or potassium hydrate.



The addition of alcohol and violent agitation facilitate the formation of this precipitate. This should be compared with a similar one under ammonium.

3. A fragment of potassium salt on the loop of a platinum wire, held in the colorless flame of a Bunsen gas lamp imparts a violet color. This reaction is interfered with by the presence of sodium salts, which color the flame yellow; organic matter also colors the flame violet, and should be removed by ignition before testing for potassium. The yellow rays of sodium may be destroyed by viewing the flame through blue glass.

4. Potassium salts are not volatile at a low red heat; at a white heat they are slowly volatilized.

REACTIONS OF SODIUM (Na).

Use a solution of sodium chloride (NaCl).

1. Sodium salts color the gas flame yellow; so delicate is this reaction that the merest traces are revealed by it.
2. The salts of sodium are not volatile at a low red heat, but slowly volatilize at a white heat.

REACTIONS OF LITHIUM (Li).

Use a solution of lithium chloride (LiCl).

1. Na_2HPO_4 added to a strong solution produces, on boiling, a white precipitate of **lithium phosphate**— Li_3PO_4 .



This reaction takes place more readily when the solution is first made alkaline with NH_4OH .

2. Lithium salts impart an intense crimson color to the gas flame. This is somewhat interfered with by sodium salts, but the yellow color of sodium may be excluded by blue glass, which if not too dark will allow the crimson rays of lithium to pass through. These must not be confused with the violet potassium rays, which will pass through a deep blue glass.

3. Lithium salts do not volatilize at a low red heat, but are slowly volatilized at a white heat.

REACTIONS OF AMMONIUM (NH_4).

Use a solution of ammonium chloride (NH_4Cl).

1. PtCl_4 produces, in strong solution, a yellow crystalline precipitate of **ammonium platino-chloride**— $(\text{NH}_4)_2\text{PtCl}_6$.

2. NaOH , added to the ammonium chloride solution and the mixture heated, causes the evolution of ammonia— NH_3 . This NH_3 is detected by the odor; by holding near a glass rod moistened with HCl , which will produce dense white fumes of NH_4Cl ; or by holding in the mouth of the tube a strip of moistened red litmus paper, when it will immediately become blue. Care must be taken, in this last test, to prevent any of the alkaline liquid coming in contact with the paper, as it would likewise cause the blue color.

3. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, added to a concentrated solution, produces a white precipitate of acid ammonium tartrate— $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$, soluble in slight excess of water.

4. Ammonium salts are volatile at a low red heat.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP I.

	K	Na	Li	NH_4
PtCl_4	Yellow Precipitate	No Precipitate	No Precipitate	Yellow Precipitate
$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	White Precipitate	No Precipitate	No Precipitate	White Precipitate
Flame	Violet	Yellow	Crimson	None
Volatility	Not Volatile	Not Volatile	Not Volatile	Volatile

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP I.

To a small portion of the solution add NaOH and heat: NH_3 will be given off if ammonium salts are present, and may be detected by the odor, or by moistened red litmus paper.

Evaporate another portion of the solution to dryness, transfer to a porcelain crucible, and heat until the white fumes of ammonium salts cease to be given off. Dissolve the residue in a few drops of H_2O with a drop or two of HCl , and add PtCl_4 ; K, if present, will be precipitated.

A loop of platinum wire dipped in the original solution and held in the colorless gas flame will give evidence of Na and Li.

If Na be present in excess, so as to obscure the Li flame, evaporate a portion of the original solution to a very small bulk, add Na_2HPO_4 and NH_4OH and boil, filter off the Li_3PO_4 , wash with hot water containing NH_4OH until the washings cease to impart a yellow color to the flame, and dissolve the precipitate in a few drops of HCl . With this solution Li may be detected by the flame test.

GROUP II.—BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

REACTIONS OF BARIUM (Ba).

Use a solution of barium chloride (BaCl₂).

1. H₂SO₄ produces an immediate precipitate of **barium sulphate**—BaSO₄, insoluble in boiling hydrochloric or nitric acid.



2. K₂CrO₄, even in dilute solutions, causes a yellow precipitate of **barium chromate**—BaCrO₄, soluble in hydrochloric or nitric acid, but insoluble in acetic acid.



3. (NH₄)₂CO₃ precipitates white **barium carbonate**—BaCO₃, soluble in acetic acid.



4. (NH₄)₂HPO₄ produces a white precipitate of **barium phosphate**—BaHPO₄, soluble in acetic or hydrochloric acid.



5. (NH₄)₂C₂O₄ causes a white precipitate of **barium oxalate**—BaC₂O₄, slightly soluble in acetic acid. This precipitation will not take place in very dilute solutions.



6. A loop of platinum wire moistened with the solution colors the gas flame green when held in it.

REACTIONS OF STRONTIUM (Sr).

Use a solution of strontium nitrate (Sr(NO₃)₂).

1. H₂SO₄ forms a white precipitate of **strontium sulphate**—SrSO₄ immediately, if the solution be strong, but not until after some time, if it be very dilute.

2. K₂CrO₄ produces no precipitate in the presence of acetic acid, but if the solution be made alkaline with KOH, a yellow precipitate, **strontium chromate**—SrCrO₄, falls.

3. (NH₄)₂CO₃ produces a white precipitate of **strontium carbonate**—SrCO₃, soluble in acetic and the stronger acids, Na₂CO₃ produces the same precipitate.

4. $(\text{NH}_4)_2\text{HPO}_4$ forms a white precipitate of **strontium phosphate**— SrHPO_4 , soluble in acids.

5. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ causes the precipitation of white **strontium oxalate**— SrC_2O_4 , sparingly soluble in acetic acid, but readily soluble in HCl .

6. Strontium salts impart an intense red to the colorless gas flame.

REACTIONS OF CALCIUM (Ca).

Use a solution of calcium chloride (CaCl_2).

1. H_2SO_4 in moderately dilute solutions, forms a white precipitate of **calcium sulphate**— CaSO_4 , soluble in excess of water.

2. $(\text{NH}_4)_2\text{CO}_3$ or Na_2CO_3 produces a white precipitate of **calcium carbonate**— CaCO_3 , soluble in acids. This precipitation is not complete unless the solution is boiled.

3. $(\text{NH}_4)_2\text{HPO}_4$ causes the precipitation of **calcium phosphate**— CaHPO_4 , soluble in acetic and the stronger acids.

4. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ produces a white precipitate of **calcium oxalate**— CaC_2O_4 , insoluble in acetic acid, soluble in hydrochloric or nitric acid.

5. The salts of calcium color the flame yellowish-red.

REACTIONS OF MAGNESIUM (Mg).

Use a solution of magnesium sulphate (MgSO_4).

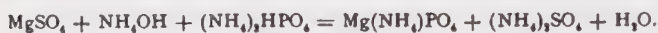
1. $(\text{NH}_4)_2\text{CO}_3$ forms a white precipitate of **magnesium-ammonium carbonate**— $\text{MgCO}_3(\text{NH}_4)_2\text{CO}_3$, soluble in NH_4Cl . By preceding the addition of the reagent by that of NH_4Cl , a much smaller quantity will suffice to keep the precipitate in solution than will be required to dissolve it after once formed.



2. KOH , NaOH or NH_4OH produces a white precipitate of **magnesium hydrate**— $\text{Mg}(\text{OH})_2$, soluble in NH_4Cl .

3. $(\text{NH}_4)_2\text{HPO}_4$ with NH_4Cl and NH_4OH produces a white crystalline precipitate of **ammonium-magnesium phosphate**— $\text{Mg}(\text{NH}_4)\text{PO}_4$, slightly soluble in water, but almost insoluble in water containing NH_4OH . Violent agitation or stirring

assists in the formation of this precipitate. $(\text{NH}_4)_2\text{HAsO}_4$ under similar circumstances precipitates white $\text{Mg}(\text{NH}_4)\text{AsO}_4$.



The ammonium chloride takes no part in the reaction, except to keep magnesium hydrate from precipitating.

4. Magnesium salts impart no color to the flame.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP II.

	Ba	Sr	Ca	Mg
H_2SO_4	White Precipitate insoluble in acids	White Precipitate insoluble in acids	White Precipitate soluble in excess of H_2O	No Precipitate
K_2CrO_4	Yellow Precipitate insoluble in acetic acid	No Precipitate unless alkaline	No Precipitate	No Precipitate
$(\text{NH}_4)_2\text{CO}_3$	White Precipitate	White Precipitate	White Precipitate	White Precipitate soluble in NH_4Cl
$(\text{NH}_4)_2\text{HPO}_4$	White Precipitate	White Precipitate	White Precipitate	White Precipitate
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	White Precipitate in strong solution	White Precipitate in strong solution	White Precipitate in dilute solution	No Precipitate unless concentrated
NH_4OH	No Precipitate	No Precipitate	No Precipitate	White Precipitate

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP II.

Add NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, boil and filter.

Ppt. Ba, Sr, Ca. Wash, dissolve in HCl , add K_2CrO_4 , filter.		Filt. Mg Allow to cool, add $(\text{NH}_4)_2\text{HPO}_4$, agitate. White ppt. if Mg be present.	
Ppt. Ba. Yellow.	Filtrate Sr, Ca. Add very dilute H_2SO_4 , allow to stand 10 minutes, filter.		
	Ppt. Sr. Confirm by flame test in original solution.	Filt. Ca. Add NH_4OH and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, white ppt.	

In order to thoroughly acquaint the student with the method of analysis by this and subsequent charts, the following explanation is given, in the belief that a careful study of it, until perfectly understood, will enable the student to follow all the charts which come after, and which are simply enlargements of this scheme.

To a small quantity of the solution in a test tube add an

equal volume of solution of NH_4Cl , close and invert the tube, so as to thoroughly mix the contents, add NH_4OH until, after mixing, the solution smells distinctly of it, and then add $(\text{NH}_4)_2\text{CO}_3$, boil and filter.

We suppose all four of the bases under consideration to be present until their absence is proven; so by this treatment we divide it into two groups. The *precipitate* consists of Ba, Sr and Ca, and the *filtrate* of Mg. A little more $(\text{NH}_4)_2\text{CO}_3$ should be added to this filtrate and the whole again boiled, to make sure that all the insoluble carbonates have been precipitated. If this is found to be the case, $(\text{NH}_4)_2\text{HPO}_4$ is added to the filtrate when cold, and Mg, if present, will form a white precipitate.

The first precipitate, consisting of Ba, Sr and Ca, having, in the meantime, been washed by forcing a jet of water from the wash bottle on it, is dissolved in $\text{HC}_2\text{H}_3\text{O}_2$, and to the solution, diluted with an equal bulk of water, K_2CrO_4 added; this again divides the solution into a precipitate and a filtrate. The yellow precipitate represents Ba, while the filtrate contains the Sr and Ca. To this filtrate *very dilute* H_2SO_4 (made by adding a small quantity of H_2SO_4 to about ten times its volume of water) is added, and the mixture allowed to stand ten minutes, for the SrSO_4 to form and subside, then filtered, which again gives a precipitate, representing Sr, and a filtrate indicating, after the addition of NH_4OH and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, the presence or absence of Ca.

DIRECTIONS FOR THE ANALYSIS OF A SOLUTION CONTAINING
SOLUBLE SALTS OF ALL THE PRECEDING ELEMENTS.

Add NH_4Cl , NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, boil and filter.

Ppt. Ba, Sr, Ca. Wash, dissolve in $\text{HC}_2\text{H}_3\text{O}_2$,* add K_2CrO_4 , filter.			† Filtrate Mg, K, Na, Li, NH_4 . Allow to cool, add $(\text{NH}_4)_2\text{HPO}_4$, agitate, filter.	
Ppt. Ba. Yellow.	Filtrate Sr, Ca. Add very dilute H_2SO_4 , allow to stand, filter.		Ppt. Mg.	Filtrate K, Na, Li, NH_4 . Evaporate to dryness, ignite, dissolve in a small quantity of H_2O , add Na_2HPO_4 , boil, filter.
	Ppt. Sr.	Filt. Ca. Add NH_4OH and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, white ppt.		
			Ppt. Li. Confirm by flame test.	Filtrate K, Na, NH_4 . Concentrate, add HCl and PtCl_4 yellow ppt. = K. Test for Na and NH_4 in original solution.

* Apply flame test to this acetic acid solution for Sr

† When sodium is absent Li may be detected by flame test.

PRECAUTIONS TO BE OBSERVED IN THE PRECEDING CHARTS.

Ammonium chloride must be added in excess, in order to keep the magnesium salts in solution when the hydrate and carbonate are added. **Ammonium hydrate** is added until the liquid smells of it. **Ammonium carbonate** is added as long as a precipitate is produced. In order to determine this to a certainty, a portion of the filtrate is tested with a little more of the reagent, when, if no precipitate occurs, the analysis may be proceeded with. This precaution of applying more of the reagent to a portion of the filtrate, to prove the complete precipitation, should be exercised in every case, as it is important to add just sufficient of the reagent to accomplish the object, but always to avoid a large excess.

**GROUP III.—MANGANESE, ZINC, COBALT,
NICKEL.**

REACTIONS OF MANGANESE (Mn).

Use a solution of manganous sulphate (MnSO₄).

1. NH₄HS, in neutral or alkaline solution, precipitates the flesh-colored **manganous sulphide**—MnS, which, on exposure to air, becomes brown. HCl, HNO₃ and HC₂H₃O₂ dissolve this precipitate, but it is insoluble in alkalies. NH₄Cl facilitates the separation of the precipitate, while the salts of the organic acids and excess of NH₄OH prevent it.

2. KOH or NaOH produces a whitish precipitate of **manganous hydrate**—Mn(OH)₂, *insoluble* in excess.



3. NH₄OH likewise precipitates Mn(OH)₂, first white, but becoming rapidly brown, *partly soluble* in excess. This precipitation is prevented by the previous addition of NH₄Cl.

4. (NH₄)₂CO₃ produces a white precipitate of **manganous carbonate**—MnCO₃, soluble in excess in the cold, but re-precipitated on warming.

5. HNO₃ and red oxide of lead will, on heating and allowing the precipitate to subside, impart to the supernatant liquid a red color, due to **permanganic acid**—H₂Mn₂O₈. Hydro-

chloric acid and chlorides interfere with this reaction. This is known as Crum's process for detecting manganese.

6. A fragment of a manganese salt fused on platinum foil with K_2CO_3 and KNO_3 will form a green mass containing **potassium manganate**— K_2MnO_4 .

7. A borax bead (formed by fusing on the loop of a platinum wire some borax until it becomes a clear glass) with manganese, in the oxidizing blowpipe flame, becomes violet while hot, and a fine amethyst color on cooling.

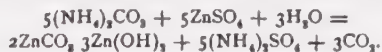
REACTIONS OF ZINC (Zn).

Use a solution of zinc sulphate ($ZnSO_4$).

1. NH_4HS produces a white precipitate of **zinc sulphide**— ZnS , insoluble in acetic acid, readily soluble in dilute hydrochloric acid.

2. KOH , $NaOH$ and NH_4OH give white precipitates of **zinc hydrate**— $Zn(OH)_2$, readily soluble in excess, forming zincates as $Zn(OK)_2$. $Zn(OH)_2$ is again precipitated on boiling.

3. $(NH_4)_2CO_3$ forms a white precipitate of **basic zinc carbonate**— $(ZnCO_3)_2(Zn(OH)_2)_3$, readily *soluble* in excess.



4. K_2CO_3 or Na_2CO_3 produces a similar precipitate, *insoluble* in excess.

5. On charcoal, before the blowpipe, metallic zinc volatilizes and burns, forming an incrustation of oxide, which is yellow while hot, becoming white on cooling; if this coating be moistened with a drop of cobaltous nitrate, and again heated in the outer flame, it becomes *green*.

REACTIONS OF COBALT (Co).

Use a solution of cobaltous nitrate ($Co(NO_3)_2$).

1. NH_4HS produces a black precipitate of **cobaltous sulphide**— CoS , insoluble in acetic acid and cold dilute hydrochloric acid. The precipitation is promoted by the presence of NH_4Cl .



2. KOH or NaOH produces a blue precipitate of **cobaltous hydrate**— $\text{Co}(\text{OH})_2$, *insoluble* in excess, and becoming pink on boiling or exposure to air.

3. NH_4OH causes a similar precipitate of $\text{Co}(\text{OH})_2$, *soluble* in excess with a red color. Sugar and some other organic compounds prevent the precipitation by the alkalies. The alkaline carbonates behave like their respective hydrates.

4. KCN gives a red brown precipitate of **cobaltous cyanide**— $\text{Co}(\text{CN})_2$, soluble in excess and reprecipitated by HCl; if, however, the solution be boiled with only a few drops of HCl, the cobaltous cyanide will not be precipitated on the further addition of HCl, on account of the formation of **potassium cobalti-cyanide**— $\text{K}_4\text{Co}_2(\text{CN})_{12}$. *This experiment should be performed in a fume closet, in order to avoid inhaling the fumes of hydrocyanic acid.*

5. Salts of cobalt color the borax bead *blue* before the blowpipe.

REACTIONS OF NICKEL (Ni).

Use a solution of nickelous sulphate (NiSO_4).

1. NH_4HS forms a black precipitate of **nickelous sulphide**— NiS , insoluble in acetic acid and cold dilute hydrochloric acid. The precipitation is promoted by the presence of NH_4Cl .

2. KOH or NaOH produces a green precipitate of **nickelous hydrate**— $\text{Ni}(\text{OH})_2$, *insoluble* in excess.

3. NH_4OH gives a similar precipitate, *soluble* in excess, with a blue color. Sugar and some other organic compounds prevent the precipitation by the alkalies. The alkaline carbonates behave like their respective hydrates.

4. KCN produces a yellowish-green precipitate of **nickelous cyanide**— $\text{Ni}(\text{CN})_2$, soluble in excess, and reprecipitated by HCl even after boiling, also precipitated, after adding HCl and boiling, by KOH. This is used as a method of distinguishing and separating nickel and cobalt, the latter *not* precipitating under these circumstances with KOH. *This experiment should be performed in a fume closet.*

5. The salts of nickel color the borax bead violet while hot, and reddish-brown when cold.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP III.

	Mn	Zn	Co	Ni
NH ₄ HS	Flesh colored precipitate.	White precipitate	Black precipitate	Black precipitate
KOH	White precipitate insoluble in excess	White precipitate soluble in excess	Blue precipitate insoluble in excess	Green precipitate insoluble in excess
NH ₄ OH	White precipitate soluble in excess	White precipitate soluble in excess	Blue precipitate soluble in excess	Green precipitate soluble in excess
(NH ₄) ₂ CO ₃	White precipitate soluble in excess	White precipitate soluble in excess	Blue precipitate soluble in excess	Green precipitate soluble in excess

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP III.

Mn, Zn, Co, Ni. Add NH₄OH, then acidify slightly with HC₉H₇O₃, warm and add H₂S until the liquid smells strongly, filter

Precipitate Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add KOH until distinctly alkaline, filter.		Filtrate Mn Add NH ₄ OH and H ₂ S. Flesh-colored ppt.
Precip. Co, Ni. Wash, dissolve in HCl, evaporate excess of acid, add KCN until the ppt first formed re-dissolves, boil with a drop or two of HCl for some minutes, and then with more HCl until all odor of HCN disappears and the reaction is acid, then evapo- rate excess of acid, add KOH until alkaline, filter.		Filt Zn Add NH ₄ HS white ppt.
Precip. Ni. Green. Confirm by dry- ing and testing with borax bead.	Filt. Co. Evaporate to dryness and test with borax bead.	

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF ALL THE ELEMENTS
PREVIOUSLY CONSIDERED.

<p style="text-align: center;">$Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4$ Add NH_4Cl, NH_4OH and NH_4HS, warm, filter.</p>		<p style="text-align: center;">Mg, K, Na, Li, NH_4 Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</p>	
<p style="text-align: center;">Wash, dissolve in HCl and HNO_3, evaporate excess of acid, add NH_4OH, acidify with H_2O_2, add H_2S, filter.</p>		<p style="text-align: center;">Filt. Mn, OH and H_2S, flame-colored ppt.</p>	
<p style="text-align: center;">Wash, dissolve in HCl and HNO_3, evaporate excess of acid, Add KOH until forming dilute, filter.</p>		<p style="text-align: center;">Wash, add H_2O_2 to H_2S, $†$ and K_2CrO_4 filter.</p>	
<p style="text-align: center;">Wash, dissolve in HCl, evaporate excess of acid and treat with K_2CO_3 and KOH until alkaline, filter.</p>		<p style="text-align: center;">Filt. Sr, Ca Add very dilute H_2SO_4, allow to stand, filter.</p>	
<p style="text-align: center;">Filt. Ni, evaporate excess of acid and treat with K_2CO_3 and KOH until alkaline, filter.</p>		<p style="text-align: center;">Filt. K, Na, Li, NH_4. Evaporate to dryness, ignite, dissolve in water, add acidity of H_2O, add Na_2HPO_4, boil filter.</p>	
<p style="text-align: center;">Filt. Co. Evaporate to dryness and test with borax bead.</p>		<p style="text-align: center;">Ppt. Mg. White.</p>	
<p style="text-align: center;">Filt. Co. Evaporate to dryness and test with borax bead.</p>		<p style="text-align: center;">Filt. K, Na, Li, NH_4. Confirm by Concentrate, add flame test, HCl and $PtCl_2$ yellow, ppt. = K. Test original solution for Na and NH_4.</p>	

* When Ni is present it may remain in solution in the NH_4HS , in which case the filtrate will be dark. To avoid this the mixture should be boiled after the addition of NH_4HS until the excess is driven off, and on filtering yields a colorless filtrate.

† Apply flame test for Sr .

GROUP IV.—IRON, CERIUM, ALUMINIUM, CHROMIUM.

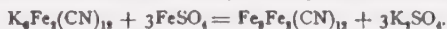
REACTIONS OF IRON *in ferrous state* (Fe)^{II}.

Use a solution of ferrous sulphate (FeSO₄).

1. K₄Fe(CN)₆, in a neutral or acid solution, gives a white (rapidly changing to light blue) precipitate of **potassium ferrous ferrocyanide**—K₂Fe₂(CN)₆, also known as Everett's salt. Alkalies decompose this precipitate, forming ferrous hydrate and a ferrocyanide of the base used.



2. K₄Fe₂(CN)₁₂, in a neutral or slightly acid solution, forms a dark blue precipitate of **ferrous ferricyanide**—Fe₃Fe₂(CN)₁₂, known as Turnbull's blue. If the solutions be very dilute there is produced merely a deep blue-green coloration.



3. KCNS produces no change.

4. H₂S in acid solution does not form a precipitate.

5. NH₄HS, with a neutral or alkaline solution, forms a black precipitate of **ferrous sulphide**, soluble in HCl or HNO₃. NH₄Cl promotes the formation of this precipitate.

6. NH₄OH in the absence of NH₄Cl produces a dirty green precipitate of **ferrous hydrate**—Fe(OH)₂. This precipitate rapidly becomes reddish-brown, owing to absorption of oxygen.

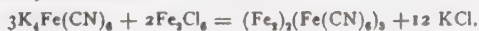
7. KOH produces a dirty green precipitate of **ferrous hydrate**—Fe(OH)₂, similar to that produced by ammonia. Non-volatile organic substances, as sugar and some acids, retard the precipitations by NH₄OH and KOH.

8. Na₂CO₃ causes a white precipitate of **ferrous carbonate**—FeCO₃, which rapidly becomes brown, from absorption of oxygen. This rapid oxidation is prevented by the use of distilled water and sugar.

REACTIONS OF IRON *in ferric state* (Fe)^{VI}.

Use a solution of ferric chloride (Fe₂Cl₆).

1. K₄Fe(CN)₆, in a neutral or acid solution, produces a dark blue precipitate of **ferric ferrocyanide**—(Fe₂)₂(Fe(CN)₆)₃, decomposed by alkalies.



2. $K_2Fe_2(CN)_{12}$ forms no precipitate, but produces a deep reddish-brown or olive-green color. The olive-green color is due to traces of ferrous salt.

3. KCNS imparts to acid solutions a deep blood-red color, due to the formation of **ferric sulphocyanate**. This color is immediately destroyed by $HgCl_2$. Dilute solutions show this reaction best.

4. H_2S forms in acid solutions a white turbidity due to separation of sulphur; the ferric salt being at the same time reduced to the ferrous condition.



In alkaline solutions this reagent acts as an alkaline sulphide.

5. NH_4HS causes a black precipitate of **ferrous sulphide**— FeS , sulphur separating at the same time.

6. NH_4OH precipitates reddish-brown **ferric hydrate**— $Fe_2(OH)_6$; non-volatile organic acids and sugar prevent this precipitation.

7. KOH and $NaOH$ react like NH_4OH .

8. Na_2CO_3 and the other alkaline carbonates precipitate **ferric hydrate**— $Fe_2(OH)_6$.

9. With borax in the oxidizing blowpipe flame, ferrous and ferric compounds give dark yellow colored beads while hot, and yellow when cold. In the reducing flame the beads change to bottle-green.

REACTIONS OF CERIUM (Ce).

Use a solution of cerous chloride (Ce_2Cl_6).

1. NH_4HS causes a white precipitate of **cerous hydrate**— $Ce_2(OH)_6$, H_2S escaping.

2. NH_4OH produces the same white precipitate of $Ce_2(OH)_6$, as also do KOH and $NaOH$.

3. $(NH_4)_2C_2O_4$ or $H_2C_2O_4$ forms a white precipitate of **cerous oxalate**— $Ce_2(C_2O_4)_3$. Organic matter does not interfere with the formation of this precipitate.

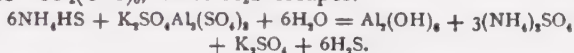
4. Na_2HPO_4 precipitates white **cerous phosphate**— $Ce_2(PO_4)_3$.

5. With a borax bead before the blowpipe the salts of cerium behave like those of iron.

REACTIONS OF ALUMINIUM (Al).

Use a solution of alum ($K_2SO_4 \cdot Al_2(SO_4)_3$).

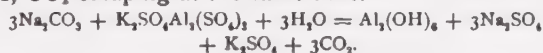
1. NH_4HS produces a white precipitate of **aluminium hydrate**— $Al_2(OH)_6$, while H_2S escapes.



2. NH_4OH forms a white precipitate of **aluminium hydrate**— $Al_2(OH)_6$, insoluble in excess; this is an important distinction from zinc.

3. KOH and $NaOH$ produce a similar white precipitate of $Al_2(OH)_6$, soluble in excess, forming aluminates of the base, as $Al_2(OK)_6$. This is not reprecipitated by boiling (distinction from chromium).

4. Na_2CO_3 and the other alkaline carbonates precipitate white gelatinous **aluminium hydrate**— $Al_2(OH)_6$, insoluble in excess, CO_2 escaping at the same time.



The presence of non-volatile organic acids and sugar prevent the complete precipitation in the above reactions.

REACTIONS OF CHROMIUM (Cr).

Use a solution of chromic chloride (Cr_2Cl_6).

1. NH_4HS produces a greenish precipitate of **chromic hydrate**— $Cr_2(OH)_6$, H_2S escaping.

2. NH_4OH forms the same greenish precipitate of $Cr_2(OH)_6$, insoluble in excess.

3. KOH and $NaOH$ produce the same precipitate soluble in excess, but reprecipitated on boiling (distinction from aluminium).

4. Na_2CO_3 and the other alkaline carbonates precipitate green basic carbonates.

5. A mixture of KNO_3 1 part and K_2CO_3 2 parts, fused with chromium compounds, become yellow from formation of **potassium chromate**— K_2CrO_4 . $AgNO_3$ and $Pb(C_2H_3O_2)_2$ are important tests for this compound; the former precipitates red **silver chromate**, the latter yellow **lead chromate**.

6. With the borax bead in the inner blowpipe flame, chromium compounds give a green color.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP IV.

	Fe(ous)	Fe(ic)	Ce	Al	Cr
$K_4Fe(CN)_6$	White ppt turning blue	Deep blue precipitate.			
$K_3Fe_2(CN)_{11}$	Deep blue precipitate	Olive-green or brownish-red color			
KCNS	No change.	Blood-red color.			
NH_4HS	Black ppt.	Black ppt.	White ppt.	White ppt	Greenish ppt.
NH_4OH	Dirty green ppt.	Reddish-brown ppt.	White ppt.	White ppt. insoluble in excess.	Greenish ppt. in soluble in excess
KOH	Dirty green ppt.	Reddish-brown ppt.	White ppt.	White ppt. soluble in excess, not reprecipitated by boiling.	Green ppt. soluble in excess, reprecipitated by boiling.
Na_2CO_3	White ppt becoming dark.	Reddish-brown ppt.	White ppt.	White ppt	Green ppt.

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP IV.

Evaporate a portion of the solution to dryness, fuse on platinum foil with a mixture of 3 parts Na_2CO_3 and 1 part KNO_3 , boil with water and filter

Residue, Fe, Ce Dissolve in concentrated H_2SO_4 5 drops, and C_2H_5OH 20 drops, dilute with water, filter and divide in two parts.		Filtrate, Al, Cr Yellow if Cr be present, divide in two parts.	
Fe. Test with $K_4Fe(CN)_6$ Test original solution with $K_4Fe(CN)_6$ and $K_3Fe_2(CN)_{11}$ for Fe(ous) and Fe(ic).	Ce. Add $H_2C_2H_3O_2$, NH_4OH and Na_2HPO_4 , white ppt	Al Add NH_4Cl and warm, white gelatinous ppt	Cr Add $H_2C_2H_3O_2$ and $Pb(C_2H_3O_2)_2$, yellow ppt.

PRECAUTIONS AND OBSERVATIONS ON THE PRECEDING CHART.

1. It is particularly desirable not to filter immediately after adding NH_4HS in the first precipitation; otherwise, the Mn will not be thoroughly precipitated.

2. When the first precipitate is dissolved in HCl and HNO_3 , great care must be exercised to thoroughly oxidize the Fe by boiling with the HNO_3 , otherwise, the precipitation by NH_4OH will not be complete.

3. The precipitate of aluminium hydrate is difficult to observe, as it floats in the solution instead of falling to the bottom. Warming the solution will usually render it visible.

4. When phosphoric acid is present, the members of Group II precipitate with Group IV, and require an entirely different method of separation. It is desirable, however, for the student first to familiarize himself with these simpler soluble salts, and undertake the more difficult cases of salts insoluble in water after the acids have been considered. See page 88.

GROUP V.—ARSENIC, ANTIMONY, TIN, GOLD, PLATINUM.

REACTIONS OF ARSENIC (As).

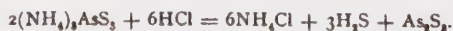
(a) ARSENIOS COMPOUNDS.

Use a solution of As_2O_3 , in water.

1. H_2S passed into the solution produces a yellow color, but no precipitate until HCl is added, when a yellow precipitate of **arsenious sulphide**— As_2S_3 , falls. This precipitate is insoluble in strong HCl , but soluble in NH_4HS , NH_4OH and $(\text{NH}_4)_2\text{CO}_3$



2. NH_4HS causes the formation of **arsenious sulphide**, which remains in solution as **ammonium sulpharsenite**— $(\text{NH}_4)_3\text{AsS}_3$. On the addition of HCl arsenious sulphide is precipitated.



3. AgNO_3 produces no precipitate until a few drops of dilute ammonia solution are added, when a yellow precipitate

of **silver arsenite**— Ag_3AsO_3 , falls, soluble in HNO_3 and in NH_4OH .

4. CuSO_4 , under similar circumstances, produces a yellowish-green precipitate of **cupric arsenite**— CuHAsO_3 .

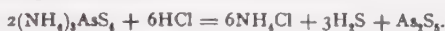
(b) ARSENIC COMPOUNDS.

Use a solution of sodium arsenate (Na_2HAsO_4).

1. H_2S causes, in acid solution only, a yellow precipitate of **arsenious sulphide**— As_2S_3 , mixed with sulphur. This reaction takes place slowly, but is accelerated by heat.



2. NH_4HS produces no precipitate, but forms **arsenic sulphide**— As_2S_3 , which remains in solution as **ammonium sulpharsenate**— $(\text{NH}_4)_3\text{AsS}_4$. Upon the addition of HCl As_2S_3 is precipitated, and not As_2S_5 and S .



3. AgNO_3 with a small amount NH_4OH , produces a chocolate-colored precipitate of **silver arsenate**— Ag_3AsO_4 , soluble in HNO_3 and NH_4OH .

4. CuSO_4 , under similar circumstances, forms a bluish-green precipitate of **cupric arsenate**— CuHAsO_4 .

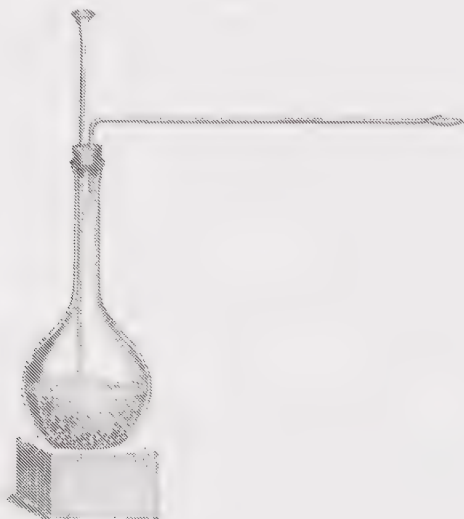
The following tests are applicable to both arsenious and arsenic compounds.

1. *Marsh's Test*.—Generate hydrogen in the usual way, allowing it to escape through a glass tube drawn out at the end so as to form a small orifice (Fig. 4). In very exact cases, the gas should be dried by passing over calcium chloride. When all the air has been expelled (which should be determined by collecting a small test tube full and holding its mouth to a flame; if the gas burn quietly, without explosion, it is pure), ignite the escaping gas; it should burn with a colorless or yellow flame; in the latter case it is due to the sodium in the glass. A piece of cold porcelain—a small crucible lid is best—is pressed down on the flame; there should be no deposit on it. Add now, through the funnel tube, a solution of arsenic, washing it down with a little water. The flame will become of a pale blue color, due to the formation of **hydrogen arsenide**— H_3As . On bringing the crucible lid

into the flame now, a blackish-brown deposit, with metallic lustre, will form on it. This deposit is readily soluble in a solution of sodium or calcium hypochlorite.

2. *Reinsch's Test*.—Boil some strips of copper with dilute HCl; if no discoloration of the copper takes place, the arsenic solution may be added. The copper immediately becomes coated with an iron-gray metallic film. Pour off the liquid, dry the copper by holding it in the lamp with the fingers so it may not become too hot, place in a clean,

FIG. 4.



dry, narrow test tube, and heat gently, when a white ring of As_2O_3 will form on the tube above the copper, readily distinguished by the characteristic octahedral shape of the crystals.

3. *Fleitman's Test*.—Generate hydrogen in a test tube with zinc and solution of potassium hydrate; moisten a piece of filter paper with one drop of solution of silver nitrate, place it over the mouth of the tube and heat; there should be no coloration of the spot on the paper. Now add some com-

pound of arsenic; the silver nitrate will immediately become black, owing to production of metallic silver.



Before the blowpipe, on charcoal, arsenic volatilizes, with the characteristic odor of garlic.

REACTIONS OF ANTIMONY (Sb).

Use a solution of tartar emetic ($\text{KSbOC}_4\text{H}_4\text{O}_6$) *acidified with HCl.*

1. H_2S forms an orange precipitate of **antimonous sulphide**— Sb_2S_3 , soluble in NH_4HS , and in concentrated HCl , but insoluble in $(\text{NH}_4)_2\text{CO}_3$.

2. NH_4HS produces an orange precipitate of **antimonous sulphide**, readily soluble in excess, forming **ammonium sulph-antimonite**— $(\text{NH}_4)_3\text{SbS}_3$, from which HCl again precipitates Sb_2S_3 .

3. KOH or NaOH precipitates white, bulky **antimonous hydrate**— $\text{Sb}(\text{OH})_3$, soluble in excess.

4. NH_4OH precipitates the same compound insoluble in excess.

4. *Marsh's Test* gives the same result as with arsenic; the black spot, however, is *insoluble* in sodium or calcium hypochlorite solution, but *soluble* in NH_4HS .

6. *Reinsch's Test* causes a deposit on copper, as with arsenic, but when heated in a tube there is formed a white amorphous ring, which is readily distinguished from the crystalline one of arsenic.

7. *Fleitman's Test* gives no result with antimony compounds.

8. On charcoal, with Na_2CO_3 , before the blowpipe, a metallic globule of antimony is produced, while characteristic fumes of the oxide are given off.

REACTIONS OF TIN (Sn).

(a) STANNOUS COMPOUNDS.

Use a solution of stannous chloride (SnCl_2).

1. H_2S precipitates dark brown **stannous sulphide**— SnS , soluble in concentrated HCl and in $(\text{NH}_4)_2\text{S}$, insoluble in NH_4HS .

2. KOH or NaOH precipitates white **stannous hydrate**— $\text{Sn}(\text{OH})_2$, *soluble* in excess; on boiling this solution SnO precipitates.

3. NH_4OH precipitates the same compound, *insoluble* in excess.

4. HgCl_2 causes a white precipitate of Hg_2Cl_2 , converting the SnCl_2 into SnCl_4 .



This precipitate blackens on the addition of NH_4OH .

(b) STANNIC COMPOUNDS.

Use a solution of stannic chloride (SnCl_4).

1. H_2S produces a yellow precipitate of **stannic sulphide**— SnS_2 , *soluble* in NH_4HS and in concentrated HCl .

2. KOH or NaOH precipitates white **stannic acid**— H_2SnO_3 , *soluble* in excess; on boiling no reprecipitation takes place—*distinction from stannous salts*.

3. NH_4OH produces the same precipitate, *insoluble* in excess.

4. Heated on charcoal, before the blowpipe, with Na_2CO_3 , metallic tin is formed, with the production of a white incrustation of the oxide.

REACTIONS OF GOLD (Au).

Use a solution of auric chloride (AuCl_3).

1. H_2S precipitates black **auric sulphide**— Au_2S_3 , *insoluble* in HCl , *soluble* in $(\text{NH}_4)_2\text{S}$.

2. $\text{H}_2\text{C}_2\text{O}_4$ or FeSO_4 precipitates metallic gold as a finely divided brown powder.

3. SnCl_2 mixed with SnCl_4 (prepared by SnCl_2 and chlorine water) produces a purple-red precipitate or coloration (Purple of Cassius), consisting of the mixed oxides of gold and tin.

4. Heated on charcoal, before the blowpipe, metallic gold is produced.

REACTIONS OF PLATINUM (Pt).

Use a solution of platonic chloride (PtCl_4).

1. H_2S causes a brown precipitate of **platonic sulphide** PtS_2 , *insoluble* in HCl , *soluble* in $(\text{NH}_4)_2\text{S}$.

2. KCl produces a yellow crystalline precipitate of **potassium platinum chloride**— K_2PtCl_6 .

3. NH_4Cl forms a similar precipitate of $(NH_4)_2PtCl_6$. The precipitation in both cases is facilitated by the addition of alcohol.

4. Zn, Fe and some other metals precipitate metallic platinum.

5. Heating on charcoal, before the blowpipe, produces the metal.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP V

	As	Sb	Sn	Au	Pt
H_2S	Yellow ppt. soluble in NH_4HS .	Orange-red ppt. soluble in NH_4HS	Brown or Yellow ppt. soluble in $(NH_4)_2S$.	Black ppt. soluble in $(NH_4)_2S$.	Brown ppt. soluble in $(NH_4)_2S$
KOH	No change.	White ppt. soluble in excess.	White ppt. soluble in excess.	No change	With excess of HCl yellow ppt.
NH_4OH	No change.	White ppt. insoluble in excess.	White ppt. insoluble in excess	Red ppt. fulminating gold.	With excess of HCl yellow ppt
Marsh's Test.	Black spot with metallic lustre, soluble in $Ca(OCl)_2$	Black, sooty spot, soluble in NH_4HS , insoluble in $Ca(OCl)_2$			
Reinsch's Test.	White sublimate of octahedral crystals	White amorphous sublimate.			
Fleissman's Test.	Dark spot of metallic silver.	No change.			

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP V.

Add HCl and H_2S , collect the precipitate, transfer to a dish, boil with concentrated HCl, filter

Ppt. As, Au, Pt If yellow, As only is present, if dark, wash, digest with $(NH_4)_2CO_3$, filter.		Filt. Sb, Sn Dilute with H_2O , boil in a dish with a strip of platinum foil, and a small piece of zinc so the metals touch. The platinum will be coated with black Sb, while the Sn will be deposited as a black sediment. This black sediment is dissolved in strong HCl and tested with $HgCl_2$, white ppt. if Sn be present. Treat the foil with a few drops of HNO_3 , dissolve in solution $H_2C_4H_7O_6$, add H_2S , orange ppt. if Sb be present	
Ppt. Au, Pt Dissolve in HCl and HNO_3 . Divide in two parts.	Filt. As Acidify with HCl, yellow ppt.		
Au Add $SnCl_2$, purple Confirm by testing original solution	Pt Add KCl, yellow ppt. Confirm by testing original solution		

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS
OF ALL THE ELEMENTS HERETOFORE CONSIDERED.

Ppt. As, Sb, Sn, Au, Pt. Wash, boil with concentrated HCl, filter.	As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH ₄ . Add HCl and H ₂ S until, after warming, the liquid smells strongly, filter.			
Ppt. As, Sb, Sn, Au, Pt. Separate by the preceding Chart for Group V. Group V.	Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add NH ₄ OH in excess, filter.			
Ppt. As, Sb, Sn, Au, Pt. Separate by the preceding Chart for Group V. Group V.	Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add NH ₄ OH in excess, filter.	Filt. Mn, Zn, Co, Ni. Acidify with HCl, H ₂ O ₂ , add H ₂ S, filter.	Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH ₄ . Evaporate to remove NH ₄ HS, add (NH ₄) ₂ CO ₃ , boil, filter.	Filt. Mg, K, Na, Li, NH ₄ . Add (NH ₄) ₂ HPO ₄ , agitate, filter.
Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add NH ₄ OH in excess, filter.	Ppt. Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, treat with KCN and HCl according to page 45, add KOH until alkaline, filter.	Filt. Mn, Zn, Co, Ni. Add NH ₄ OH and H ₂ S. Fish-colored ppt.	Ppt. Ba, Sr, Ca, Mg, K, Na, Li, NH ₄ . Wash, dissolve in HCl, H ₂ O ₂ , add H ₂ S, filter.	Filt. K, Na, Li, NH ₄ . Wash, dissolve in HCl, H ₂ O ₂ , add H ₂ S, filter.
Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add NH ₄ OH in excess, filter.	Filt. Al, Cr. Yellow if Cr be present, divide in two parts.	Filt. Zn, Co, Ni. Add NH ₄ HS. White ppt.	Filt. Sr, Ca, Mg, K, Na, Li, NH ₄ . Add very dilute H ₂ SO ₄ , allow to stand, filter.	Filt. K, Na, Li, NH ₄ . Wash, dissolve in HCl, H ₂ O ₂ , add H ₂ S, filter.
Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add NH ₄ OH in excess, filter.	Al, Add NH ₄ Cl and HCl, white ppt.	Filt. Co, Ni. Add NH ₄ HS. White ppt.	Filt. Ca, Mg, K, Na, Li, NH ₄ . Add very dilute H ₂ SO ₄ , allow to stand, filter.	Filt. K, Na, Li, NH ₄ . Wash, dissolve in HCl, H ₂ O ₂ , add H ₂ S, filter.
Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni. Wash, dissolve in HCl and HNO ₃ , evaporate excess of acid, add NH ₄ OH in excess, filter.	Cr, Add HCl and HCl, yellow ppt.	Filt. Co, Ni. Add NH ₄ HS. White ppt.	Filt. Sr, Ca, Mg, K, Na, Li, NH ₄ . Add very dilute H ₂ SO ₄ , allow to stand, filter.	Filt. K, Na, Li, NH ₄ . Wash, dissolve in HCl, H ₂ O ₂ , add H ₂ S, filter.

PRECAUTIONS AND OBSERVATIONS ON THE PRECEDING CHART.

A great deal of time may be saved by carefully noting the color of the precipitate produced by H_2S . If stannic salts are absent and the precipitate yellow, As only is present, if orange, Sb is present and As may be; when such an orange precipitate is obtained and Sn(ic) is absent, the readiest method of separation is to wash, and add to the precipitate $(NH_4)_2CO_3$. As will be dissolved, and may be detected in the filtrate by adding HCl, while the Sb remains on the filter. When the precipitate is dark, Au and Pt should be sought for in the original solution, as well as separated by the chart.

Only a small piece of zinc is necessary to effect the separation of Sn and Sb.

GROUP VI.—MERCURY (IC), BISMUTH, COPPER, CADMIUM.

REACTIONS OF MERCURY *as mercuric salt* (Hg(ic)).

. *Use a solution of mercuric chloride* ($HgCl_2$).

1. H_2S or NH_4HS produces, when in small proportion, a whitish precipitate of $(HgS)_2HgCl_2$; a further addition of the reagent, together with the application of heat, causes the formation of a black precipitate of **mercuric sulphide**— HgS , insoluble in either HCl or HNO_3 , but soluble in a mixture of the two.

2. KOH or NaOH produces a yellow precipitate of **mercuric oxide**— HgO ; unless the reagent be in excess, a brown precipitate of a basic salt is formed.



3. NH_4OH precipitates white **mercur-ammonium chloride**— NH_2HgCl .



This precipitate is readily soluble in HCl and in HCl_2 .

4. K_2CrO_4 produces a red precipitate of **mercuric chromate**— $HgCrO_4$.

5. KI precipitates **mercuric iodide**— HgI_2 , first yellow, but rapidly becoming scarlet. This precipitate is readily soluble in excess of KI or $HgCl_2$.

6. $SnCl_2$, in small quantity, in the presence of HCl, pre-

precipitates **mercurous chloride**— Hg_2Cl_2 . On the addition of a larger quantity of the reagent, the mercurous chloride is reduced to the metal, which may be collected into a globule.

7. Na_2CO_3 produces a reddish-brown precipitate of basic carbonate— $\text{HgCO}_3(\text{HgO})_2$.

8. Copper turnings boiled with the solution acidified with HCl become quickly coated with metallic mercury. The presence of HNO_3 must be avoided. If these coated turnings are carefully dried at a low temperature, placed in the bottom of a narrow test tube and heated, a ring composed of globules of mercury will form on the cool part of the tube. These minute globules may be formed into larger ones by pressing them together with a glass rod, until they may be seen with the naked eye.

9. Before the blowpipe, HgO breaks up into Hg and O . HgS , under similar circumstances, sublimes unchanged.

REACTIONS OF BISMUTH (Bi).

Use a solution of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$).

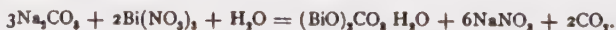
1. H_2S or NH_4HS produces a black precipitate of **bismuth trisulphide**— Bi_2S_3 , insoluble in dilute acids and alkalies, soluble in boiling HNO_3 .

2. KOH , NaOH or NH_4OH forms a white precipitate of **bismuth hydrate**— $\text{Bi}(\text{OH})_3$, converted by boiling into the yellow oxide— Bi_2O_3 .

3. K_2CrO_4 precipitates yellow **bismuth chromate**— $\text{Bi}_2(\text{CrO}_4)_3$.

4. KI forms a brown precipitate of **bismuth iodide**— BiI_3 , soluble in excess of the reagent.

5. Na_2CO_3 precipitates white **oxycarbonate of bismuth**— $(\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O}$.



6. H_2O in excess, when there is not an excess of free acid, precipitates **bismuth subnitrate**— $\text{BiONO}_3 \cdot \text{H}_2\text{O}$.



When the chloride is so diluted the **oxychloride**— BiOCl , separates.

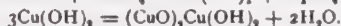
7. Bismuth on charcoal, before the blowpipe, forms a hard bead of metal, with a characteristic incrustation of oxide—deep orange-yellow while hot, pale when cold.

REACTIONS OF COPPER (Cu).

Use a solution of cupric sulphate (CuSO₄).

1. H₂S and NH₄HS precipitate black **cupric sulphide**—CuS, insoluble in dilute acids and alkalis, slightly soluble in NH₄HS, and entirely dissolved by boiling HNO₃. This precipitation is prevented by KCN.

2. KOH or NaOH produces a light blue precipitate of **cupric hydrate**—Cu(OH)₂, insoluble in excess, and converted by boiling into black **cupric oxyhydrate**—(CuO)₂Cu(OH)₂. In the presence of non-volatile organic acids this precipitation does not take place, but a blue color results.



3. NH₄OH in small quantity forms a greenish-purple precipitate, readily soluble in excess, forming **tetra-ammonio-cupric sulphate**—(NH₄)₄CuSO₄·H₂O.



4. K₄Fe(CN)₆ precipitates reddish-brown **cupric ferro-cyanide**—Cu₂Fe(CN)₆.

5. Metallic Fe or Zn precipitates red metallic Cu.

6. In the outer blowpipe flame copper salts color the borax bead green while hot, blue when cold. In the inner flame, after moistening with SnCl₂, it becomes red, owing to formation of Cu₂O.

REACTIONS OF CADMIUM (Cd).

Use a solution of cadmium sulphate (CdSO₄).

1. H₂S or NH₄HS precipitates yellow **cadmium sulphide**—CdS, soluble in hot HNO₃ and dilute H₂SO₄, but insoluble in NH₄HS or KCN.

2. KOH or NaOH produces a white precipitate of **cadmium hydrate**—Cd(OH)₂, *insoluble* in excess.

3. NH₄OH causes the same white precipitate of Cd(OH)₂, *soluble* in excess.

4. Na_2CO_3 produces a white precipitate of cadmium carbonate— CdCO_3 , *insoluble* in excess, but slightly soluble in ammonium salts, entirely soluble in NH_4OH .

5. On charcoal, before the blowpipe, the salts of cadmium are reduced to metal and volatilize, forming a brownish incrustation of oxide.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP VI.

	Hg(ic)	Bi	Cu	Cd
H_2S or NH_4HS	Black ppt. insoluble in HNO_3	Black ppt.	Black ppt. soluble in KCN .	Yellow ppt. insoluble in KCN
KOH	Yellow ppt.	White ppt.	Blue ppt	White ppt
NH_4OH	White ppt.	White ppt.	Blue ppt. soluble in excess.	White ppt soluble in excess.
Na_2CO_3	Reddish-brown ppt.	White ppt.	Blue ppt.	White ppt.

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP VI.

Add H_2S , collect the precipitate, boil it with HNO_3 , (sp gr. 1.20); filter.

Ppt. Hg. Black. Confirm by Cu, according to 8, page 60.	Filt. Bi, Cu, Cd Add NH_4OH in excess, filter.		
	Ppt. Bi.* White.	Filt. Cu, Cd. Add H_2S , collect and wash; boil with dilute H_2SO_4 (one part of concentrated acid and five parts water); filter.	
		Ppt. Cu Black.	Filt. Cd. Dilute, add H_2S , yellow ppt

* To confirm the presence of Bi, wash this precipitate, pour on it a few drops of hydrochloric acid and allow the solution thus formed to run into a test tube of water, when if the precipitate was Bi, a white precipitate of bismuth oxychloride will form.

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF ALL THE ELEMENTS HERETOFORE CONSIDERED.

<p>Ppt. Hg, Bi, Cu, Cd, As, Sb, Sn, Au, Pt. Wash, digest with $(\text{NH}_4)_2\text{S}$, filter.</p>		<p>Hg(ite), Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Co, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH₄. Add HCl and H₂S, filter.</p>		<p>Ppt. Fe, Co, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH₄. Add NH_4Cl, NH_4OH, NH_4HS, warm, filter.</p>		<p>Filt. Fe, Co, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH₄. Evaporate to dryness, add $(\text{NH}_4)_2\text{CO}_3$, filter.</p>		<p>Ppt. Ba, Sr, Ca. Wash with $\text{HC}_2\text{H}_3\text{O}_2$, add K_2CrO_4, filter.</p>		<p>Filt. Mg, K, Na, Li, NH₄. Add $(\text{NH}_4)_2\text{HPO}_4$, agitate, filter.</p>		<p>Ppt. Mg. Evaporate to dryness, ignite, dissolve in Na_2HPO_4, boil and filter.</p>		<p>Filt. K, Na, Li, NH₄. Conc. and add HCl and PtCl_4, yellow flame test. ppt. = K. Test for Na and NH₄ in original solution.</p>	
<p>Ppt. Hg, Bi, Cu, Cd, As, Sb, Sn, Au, Pt. Wash, digest with $(\text{NH}_4)_2\text{S}$, filter.</p>		<p>Filt. As, Sb, Sn, Au, Pt. Acidify with dilute HCl. Collect and precipitate (brown filtrate), boil the ppt. with concentrated HCl, filter.</p>		<p>Ppt. Fe, Co, Al, Cr. Wash, dry, fuse on Pt with KNO_3, add with Li_2O, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Acidify with $\text{HC}_2\text{H}_3\text{O}_2$, add H_2S, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Wash, dissolve in HCl and add KOH, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Wash, dissolve in HCl and add KOH, filter.</p>		<p>Ppt. Ba, Sr, Ca. Wash with $\text{HC}_2\text{H}_3\text{O}_2$, add K_2CrO_4, filter.</p>		<p>Filt. K, Na, Li, NH₄. Conc. and add HCl and PtCl_4, yellow flame test. ppt. = K. Test for Na and NH₄ in original solution.</p>	
<p>Ppt. Hg, Bi, Cu, Cd, As, Sb, Sn, Au, Pt. Wash, digest with $(\text{NH}_4)_2\text{S}$, filter.</p>		<p>Filt. As, Sb, Sn, Au, Pt. Acidify with dilute HCl. Collect and precipitate (brown filtrate), boil the ppt. with concentrated HCl, filter.</p>		<p>Ppt. Fe, Co, Al, Cr. Wash, dry, fuse on Pt with KNO_3, add with Li_2O, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Acidify with $\text{HC}_2\text{H}_3\text{O}_2$, add H_2S, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Wash, dissolve in HCl and add KOH, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Wash, dissolve in HCl and add KOH, filter.</p>		<p>Ppt. Ba, Sr, Ca. Wash with $\text{HC}_2\text{H}_3\text{O}_2$, add K_2CrO_4, filter.</p>		<p>Filt. K, Na, Li, NH₄. Conc. and add HCl and PtCl_4, yellow flame test. ppt. = K. Test for Na and NH₄ in original solution.</p>	
<p>Ppt. Hg, Bi, Cu, Cd, As, Sb, Sn, Au, Pt. Wash, digest with $(\text{NH}_4)_2\text{S}$, filter.</p>		<p>Filt. As, Sb, Sn, Au, Pt. Acidify with dilute HCl. Collect and precipitate (brown filtrate), boil the ppt. with concentrated HCl, filter.</p>		<p>Ppt. Fe, Co, Al, Cr. Wash, dry, fuse on Pt with KNO_3, add with Li_2O, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Acidify with $\text{HC}_2\text{H}_3\text{O}_2$, add H_2S, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Wash, dissolve in HCl and add KOH, filter.</p>		<p>Filt. Mn, Zn, Co, Ni. Wash, dissolve in HCl and add KOH, filter.</p>		<p>Ppt. Ba, Sr, Ca. Wash with $\text{HC}_2\text{H}_3\text{O}_2$, add K_2CrO_4, filter.</p>		<p>Filt. K, Na, Li, NH₄. Conc. and add HCl and PtCl_4, yellow flame test. ppt. = K. Test for Na and NH₄ in original solution.</p>	

PRECAUTIONS AND OBSERVATIONS ON THE PRECEDING CHART.

1. Unless excess of H_2S be used, and the solution warmed, Hg will not be thoroughly precipitated.

2. When Sn, Au and Pt are present, the yellow ammonium sulphide $(\text{NH}_4)_2\text{S}$ must be used to dissolve Group V. When Cu is present some of it may be dissolved, so that any dark precipitate in that group should be tested for Cu.

3. When the precipitate insoluble in NH_4HS is boiled with HNO_3 , a black mass of sulphur is sometimes obtained. This is readily distinguished from Hg, because it floats as one mass on the liquid, while the mercury collects at the bottom as a heavy, black precipitate.

GROUP VII.—SILVER, MERCURY(OUS), LEAD.

REACTIONS OF SILVER (Ag).

Use a solution of silver nitrate (AgNO_3).

1. HCl or soluble chlorides precipitate white, curdy **silver chloride**— AgCl , insoluble in HNO_3 , soluble in NH_4OH , forming **ammonio-silver chloride**— $(\text{AgCl})_2(\text{NH}_3)_3$, from which the chloride is again precipitated by acids.



2. H_2S or NH_4HS produces a black precipitate of **silver sulphide**— Ag_2S , insoluble in dilute acids and in alkalies, soluble in boiling HNO_3 .

3. KOH or NaOH forms a grayish-brown precipitate of **silver oxide**— Ag_2O , insoluble in excess, but soluble in NH_4OH .



4. NH_4OH in small quantity, precipitates **silver oxide**, soluble in excess.

5. K_2CrO_4 produces a red precipitate of **silver chromate**— Ag_2CrO_4 , soluble in concentrated HNO_3 and in NH_4OH .

6. KI and KBr produce precipitates of **silver iodide**— AgI , yellow, insoluble in NH_4OH , and **silver bromide**— AgBr , yellowish-white, slowly soluble in NH_4OH .

7. KCN precipitates white **silver cyanide**— AgCN , soluble in excess and in concentrated HNO_3 .

8. Heated with Na_2CO_3 on charcoal, before the blowpipe, compounds of silver form a bright, metallic button, soluble in HNO_3 .

REACTIONS OF MERCURY as mercurous salt ($\text{Hg}(\text{ous})$).

Use a solution of mercurous nitrate ($\text{Hg}_2(\text{NO}_3)_2$).

1. HCl or soluble chlorides precipitate **mercurous chloride**— Hg_2Cl_2 , converted by strong HNO_3 into a mixture of HgCl_2 and $\text{Hg}(\text{NO}_3)_2$, also becoming black on the addition of NH_4OH , forming $\text{NH}_2\text{Hg}_2\text{Cl}$.

2. H_2S or NH_4HS precipitates a mixture of Hg with HgS .

3. KOH or NaOH produces a black precipitate of **mercurous oxide**— Hg_2O , insoluble in excess.

4. NH_4OH causes a black precipitate of **mercurous-ammonium nitrate**— $\text{NH}_2\text{Hg}_2\text{NO}_3$.



5. K_2CrO_4 forms an orange precipitate of **mercurous chromate**— Hg_2CrO_4 .

6. KI precipitates green **mercurous iodide**— Hg_2I_2 .

7. Before the blowpipe, mercurous salts volatilize, some being converted into mercuric salt and mercury, both of which sublime.

REACTIONS OF LEAD (Pb).

Use a solution of lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$).

1. HCl , or soluble chlorides, produce a white precipitate of **lead chloride**— PbCl_2 , soluble in hot water.

2. H_2S or NH_4HS precipitates black **lead sulphide**— PbS , insoluble in HCl , soluble in hot HNO_3 .

3. KOH or NaOH produces a white precipitate of **lead hydrate**— $\text{Pb}(\text{OH})_2$, soluble in large excess, forming **potassium** or **sodium plumbate**— K_2PbO_2 or Na_2PbO_2 .

4. NH_4OH precipitates white **basic lead hydrate**.

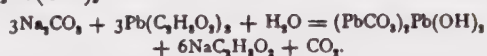
5. K_2CrO_4 produces a yellow precipitate of **lead chromate**— PbCrO_4 , soluble in KOH and in strong HNO_3 .

6. KI forms a yellow precipitate of **lead iodide**— PbI_2 , soluble in boiling water.

7. H_2SO_4 produces a white precipitate of **lead sulphate**—

PbSO_4 , insoluble in acids, but soluble in solution of ammonium acetate or tartrate.

8. Na_2CO_3 precipitates white basic lead carbonate— $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$.



9. Before the blowpipe, on charcoal, lead compounds are converted into a malleable globule of the metal, with the formation of some yellow oxide.

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP VII.

	Ag	Hg(ous)	Pb
HCl	White ppt soluble in NH_4OH	White ppt turning black with NH_4OH .	White ppt soluble in hot H_2O .
H_2S and NH_4HS	Black ppt.	Black ppt.	Black ppt.
KOH	Brown ppt.	Black ppt.	White ppt.
NH_4OH	Brown ppt.	Black ppt.	White ppt.
Na_2CO_3	Brown ppt.	Black ppt	White ppt.
K_2CrO_4	Red ppt	Orange ppt.	Yellow ppt.
KI	Yellow ppt	Green ppt.	Yellow ppt.

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP VII

Add HCl, collect, wash and pour on the filter boiling H_2O .

Ppt. Ag, Hg(ous). Pour on the filter NH_4OH .		Filt. Pb. Add dilute H_2SO_4 , white ppt.	
Ppt. Hg(ous) Black	Filt. Ag. Acidify with HNO_3 , white ppt.		

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF ALL THE ELEMENTS HERETOFORE CONSIDERED.

[illegible]

SPECIAL PRECAUTIONS TO BE OBSERVED IN THE EXAMINATION FOR BASES.

1. HCl may precipitate basic salts of Bi and Sb; these are readily distinguished from the bases of Group VII by dissolving on the further addition of HCl. It is best to make a preliminary test on a small quantity of the solution by the addition of an equal volume of dilute HCl. If no precipitate is formed, or if at first formed, is redissolved, the addition of an excess of HCl to the portion taken for analysis may be avoided.

2. The precipitation with HCl should be performed in the cold, in order to prevent the $PbCl_2$ from dissolving.

3. Before commencing the analysis of a solution its action on litmus paper should always be noted. If alkaline a precipitate may be caused by HCl, on account of the presence of substances soluble in alkalies, as As_2S_3 in $(NH_4)_2CO_3$, and $AgCl$ in NH_4OH . Or silicic acid from alkaline silicates may be precipitated, in which case it is necessary to precede the addition of HCl, by evaporation to dryness with HNO_3 , filtering out the insoluble silica, and proceeding with the filtrate in the usual way.

4. The addition of H_2S should be slow, and interrupted from time to time to warm and agitate the solution, and so continued until it smells strongly of the reagent.

5. When the presence of HNO_3 is suspected, the filtrate after the precipitation of Group VII, and before the addition of H_2S , should be evaporated to dryness to expel the HNO_3 , dissolved in water and, if necessary, acidified with HCl.

SPECIAL OBSERVATION.

The separation into groups is accomplished by the following reagents, which are called *group reagents* :—

HCl	precipitates	AgCl, Hg ₂ Cl ₂ , PbCl ₂ ,	Group VII.
		{ HgS, PbS, Bi ₂ S ₃ , CuS, CdS, insoluble in (NH ₄) ₂ S, }	Group VI.
H ₂ S	"	{ As ₂ S ₃ , Sb ₂ S ₃ , SnS, SnS ₂ , Au ₂ S ₃ , PtS ₂ , soluble in (NH ₄) ₂ S, }	Group V.
		{ FeS, Ce ₂ (OH) ₆ , Al ₂ (OH) ₆ , Cr ₂ (OH) ₆ , hydrates insoluble in NH ₄ OH, }	Group IV.
NH ₄ HS	"	{ MnS, ZnS, CoS, NiS, hydrates soluble in NH ₄ OH, }	Group III.
(NH ₄) ₂ CO ₃	"	{ BaCO ₃ , SrCO ₃ , CaCO ₃ , }	Group II.
(NH ₄) ₂ HPO ₄	"	{ MgNH ₄ PO ₄ , }	Group I.
Not precipitated in a group.	}	K, Na, Li, NH ₄ ,	Group I.

When one of these reagents fails to produce a precipitate, it indicates the absence of that group, and the next group reagent is immediately added.

SECTION II.

ACIDS.

GROUP I.—HYDROCHLORIC ACID, HYDROBROMIC ACID, HYDRIODIC ACID, HYDROCYANIC ACID, HYDROFLUORIC ACID.

REACTIONS OF HYDROCHLORIC ACID (HCl).

Use a solution of potassium chloride (KCl).

1. AgNO_3 produces a white, curdy precipitate of **silver chloride**— AgCl , insoluble in HNO_3 , readily soluble in NH_4OH .

This precipitate should be preserved to compare with those of AgBr and AgI .

2. $\text{Hg}_2(\text{NO}_3)_2$ causes a white precipitate of **mercurous chloride**— Hg_2Cl_2 , insoluble in HNO_3 , blackening on the addition of NH_4OH .

3. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ forms a white crystalline precipitate of **lead chloride**— PbCl_2 , soluble in 33 parts of boiling water.

4. Warming with H_2SO_4 and MnO_2 causes the evolution of *Chlorine*, recognized by its odor and color.

5. On warming with H_2SO_4 , **hydrochloric acid** is given off, recognized by its odor and intensely acid reaction; also by the dense white fumes of NH_4Cl produced by holding a rod moistened with NH_4OH near the mouth of the tube.

REACTIONS OF HYDROBROMIC ACID (HBr).

Use a solution of potassium bromide (KBr).

1. AgNO_3 produces a yellowish-white precipitate of **silver bromide**— AgBr , insoluble in HNO_3 , slowly soluble in NH_4OH .

This precipitate should be compared with those of AgCl and AgI .

2. HgCl_2 forms a white precipitate of **mercuric bromide**— Hg_2Br_2 , soluble in a large quantity of water.

3. $\text{Hg}_2(\text{NO}_3)_2$ precipitates yellowish-white **mercurous bromide**— Hg_2Br_2 .

4. H_2SO_4 , when concentrated, causes the evolution of red vapors of bromine; this occurs more readily in the presence of MnO_2 .

5. Chlorine water and starch paste cause a yellow color, due to formation of starch bromide; in dilute solutions it is necessary to agitate the mixture with ether or chloroform, which will separate, carrying the bromine in solution, with a yellowish-red color.

REACTIONS OF HYDRIODIC ACID (HI).

Use a solution of potassium iodide (KI).

1. AgNO_3 produces a yellowish precipitate of **silver iodide**— AgI , insoluble in HNO_3 and almost insoluble in NH_4OH .

2. $\text{Hg}_2(\text{NO}_3)_2$ precipitates green **mercurous iodide**— Hg_2I_2 .

3. HgCl_2 causes a red precipitate of **mercuric iodide**— HgI_2 , soluble in excess of either reagent.

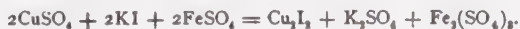
4. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ produces a yellow precipitate of **lead iodide**— PbI_2 , soluble in boiling water.

5. Chlorine water and starch paste form a blue color of starch iodide, which color disappears on heating and returns on cooling, also destroyed by excess of chlorine water.

6. A concentrated solution of CuSO_4 produces a white precipitate of **cuprous iodide**— Cu_2I_2 ,—which is colored dark by free iodine according to the following reaction:—



When a reducing agent, as FeSO_4 , is added at the same time, the liberation of iodine is prevented and the true color of the precipitate may then be seen.



This reaction is sometimes useful in separating iodine from chlorine and bromine. The reagent in this case should be a strong solution of one part CuSO_4 and three parts FeSO_4 .

HYDROFLUORIC ACID (HF).

The evolution of intensely irritating fumes of this acid, on the addition of H_2SO_4 to calcium fluoride, which etch glass, is sufficiently characteristic.

REACTIONS OF HYDROCYANIC ACID (HCN).

Use a solution of potassium cyanide (KCN).

1. AgNO_3 produces a white precipitate of AgCN , soluble in KCN , sparingly soluble in NH_4OH , and insoluble in dilute HNO_3 .

2. NH_4HS evaporated with KCN to dryness, on a water bath, will give, on dissolving in water and adding Fe_2Cl_6 , a deep blood-red color, due to formation of sulphocyanate.

3. Fe_2Cl_6 and FeSO_4 , then NaOH until a precipitate is produced, heat and add HCl , will give a deep blue ppt. of **ferric ferrocyanide** (Prussian blue).

4. HCl or any other acid causes an evolution of HCN , readily recognized by its odor. *Great care should be exercised in carrying out this test in order to avoid inhaling more than a trace of the fumes.*

SUMMARY OF TESTS WITH SOLUBLE SALTS OF GROUP I.

	HCl	HBr	HI	HCN
AgNO_3	White ppt. soluble in NH_4OH	Yellowish-white ppt. slowly soluble in NH_4OH .	Yellowish ppt. insoluble in NH_4OH .	White ppt. sparingly soluble in NH_4OH .
$\text{Hg}_2(\text{NO}_3)_2$	White ppt.	Yellowish-white ppt.	Greenish ppt.	White ppt.
HgCl_2	No ppt.	White ppt.	Red ppt.	No ppt.
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	White ppt.	White ppt.	Yellow ppt.	White ppt.
Chlorine water and starch solution.	No color.	Yellow color	Blue color.	No color.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP I.

Add HNO_3 and boil for some time; the HCN is driven off. *This operation should be performed with caution, so as to avoid inhaling these poisonous fumes.*

After all the HCN has been driven off, add AgNO_3 and shake well; collect the precipitate of AgCl , AgBr , AgI on a filter, and, after washing, pour on the filter NH_4OH ; AgCl will be dissolved, and may be detected in the filtrate by acidifying with HNO_3 .

To detect HBr and HI take another portion of the original solution; add a few drops of starch solution, and then, slowly, chlorine water, until, after agitation, the liquid smells of it. If there is a blue color HI is present. Continue the addition of chlorine water until the blue color is destroyed, when, if the solution is yellow, HBr is indicated. This may be still further verified by agitating with chloroform, which will, after separating, assume a yellowish-red color if HBr is present.

GROUP II.

HYPOCHLOROUS ACID.		HYPOPHOSPHOROUS ACID.	
CHLORIC	"	ORTHOPHOSPHORIC	"
HYDROXYL.		PYROPHOSPHORIC	"
HYDROSULPHURIC ACID.		METAPHOSPHORIC	"
SULPHUROUS	"	BORIC	"
SULPHURIC	"	CARBONIC	"
THIOSULPHURIC	"	SILICIC	"
NITRIC	"		

REACTIONS OF HYPOCHLOROUS ACID (HClO).

Use a solution of sodium hypochlorite (NaClO).

1. HCl causes the evolution of **chlorine**, readily recognized by its odor and by the bleaching action it exerts on litmus paper, or solution of indigo.
2. AgNO₃ produces a white precipitate of **silver chloride**—AgCl, soluble in NH₄OH.



3. Pb(C₂H₃O₂)₂, with an excess of the solution, forms at first a white precipitate which, on heating, turns brown, owing to formation of **lead peroxide**—PbO₂.

REACTIONS OF CHLORIC ACID (HClO₃).

Use a solution of potassium chlorate (KClO₃).

1. H₂SO₄ causes the evolution of yellow **chlorine tetroxide**—Cl₂O₄, having a characteristic odor. When the dry salt is used this reaction takes place with some violence, or when organic matter is present, with explosion.
2. On heating the dry salt in a crucible **oxygen** is given off,

readily detected by holding over the mass the glowing end of a match or taper.

3. AgNO_3 produces no precipitate. This is an important distinction from HCl and HClO . When they are present they may be removed by just enough AgNO_3 to precipitate them, and the remaining solution tested for HClO_3 by evaporating to dryness, heating to redness, dissolving in water and testing with AgNO_3 , when, if a chlorate was present, a precipitate of AgCl will form, on account of the chlorate having been converted by heat into chloride.

4. A modification of the above test may be used to distinguish a chlorate from a nitrate, as the latter gives many of the reactions of the former. The residue, after heating a nitrate, will not give a precipitate when dissolved in water and tested with AgNO_3 .

5. AgNO_3 with a drop or two of strong H_2SO_4 , will cause a white precipitate of silver chloride, AgCl , owing to the decomposition of the chlorate by the strong acid.

WATER (H_2O), HYDRATES AND OXIDES.

Water is distinguished by having no odor or taste, not changing litmus, and evaporating without residue.

The soluble hydrates KOH , NaOH , LiOH , Ca(OH)_2 , Sr(OH)_2 , Ba(OH)_2 , yield solutions with water which change red litmus paper blue. The insoluble hydrates give off steam when heated in a dry tube.

The soluble oxides K_2O , Na_2O , Li_2O , CaO , SrO , BaO , are known by forming hydrates with water. The insoluble oxides are recognized by giving negative tests for acids when dissolved and tested in the usual way.

HYDROSULPHURIC ACID (H_2S).

Sufficient evidence of the presence of this acid is afforded by the characteristic odor. In the case of sulphides, first adding H_2SO_4 and warming if necessary. A trace may be detected by holding over the mouth of the tube a piece of filter paper moistened with lead acetate, which will become black (lead sulphide) in the presence of H_2S .

REACTIONS OF SULPHUROUS ACID (H_2SO_3).

Use a solution of sodium sulphite (Na_2SO_3).

1. In solution, uncombined, the free acid is recognized by the odor of burning sulphur, by strong bleaching action, by decolorizing potassium permanganate solution, and by causing the evolution of hydrogen sulphide when added to a mixture of zinc and hydrochloric acid.
2. Sulphites are distinguished by the characteristic odor of SO_2 on the addition of a strong acid.
3. Salts of Ag, Hg or Pb, produce precipitates which blacken on heating, owing to formation of sulphides.
4. BaCl_2 with neutral solutions forms a white precipitate of **barium sulphite**— BaSO_3 , soluble in HCl .
5. With zinc and hydrochloric acid hydrogen sulphide is evolved.
6. When to a dilute solution of a sulphite, zinc sulphate and sodium nitroprusside are added, a red color is produced, or when the solution is more concentrated, a flocculent reddish precipitate falls; a few drops of potassium ferrocyanide render the reaction more distinct. This test will serve to distinguish sulphites from thiosulphates, as the latter do not cause this red color.

REACTIONS OF SULPHURIC ACID (H_2SO_4).

Use dilute H_2SO_4 , or an alkali sulphate.

1. BaCl_2 produces a white precipitate of **barium sulphate**— BaSO_4 , insoluble in boiling concentrated acids.
2. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ causes a precipitate of **white lead sulphate**, insoluble in dilute acids, but soluble in hot concentrated acids. Alcohol increases the delicacy of this reaction.
3. A sulphate fused on charcoal with Na_2CO_3 , the fused mass placed on a bright silver coin and moistened with a drop of dilute HCl will cause a black stain, due to formation of silver sulphide. This reaction is especially adapted to the detection of *insoluble* sulphates.

REACTIONS OF THIOSULPHURIC (HYPOSULPHUROUS) ACID ($\text{H}_2\text{S}_2\text{O}_3$).

Use a solution of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$).

1. H_2SO_4 causes the evolution of **sulphurous oxide**— SO_2 , recognized by the odor. A deposit of sulphur takes place at the same time, which is an important distinction from sulphites.

2. AgNO_3 produces a white precipitate of **silver thiosulphate**— $\text{Ag}_2\text{S}_2\text{O}_3$, soluble in excess. After a time (immediately on heating) the precipitate becomes dark and then black, silver sulphide and sulphuric acid being formed.

3. BaCl_2 produces a white precipitate soluble in excess of H_2O , and decomposed by HCl .

4. Added to a mixture of zinc and hydrochloric acid, hydrogen sulphide is evolved.

REACTIONS OF NITRIC ACID (HNO_3).

Use a solution of potassium nitrate (KNO_3).

1. H_2SO_4 , on heating, will cause the nitric acid to volatilize. If copper turnings be added with the sulphuric acid colorless **nitrogen dioxide**— N_2O_2 will be given off, which in contact with air will form red **nitrogen tetroxide**— N_2O_4 , readily recognized by the color and odor. If alcohol be added to the mixture, the characteristic odor of nitrous ether is developed.

2. FeSO_4 , acidified with H_2SO_4 , added in a test tube, so as to form a layer on a solution of nitrate, acidified with H_2SO_4 , will cause a dark layer to form at the line of contact.

3. Indigo solution, strongly acidified with H_2SO_4 , is decolorized by a nitrate.

4. Zinc and potassium hydrate cause the reduction of the acid to ammonia, which may be detected in the usual way. This is a valuable test for distinguishing nitric acid in the presence of chloric acid.

5. Heated on charcoal, deflagration takes place, the charcoal burning at the expense of the oxygen of the nitrate.

HYPOPHOSPHOROUS ACID (H_2PO_2).

1. By ignition the hypophosphites are resolved into spontaneously inflammable **hydrogen phosphide**— PH_3 , and phosphate.
2. AgNO_3 produces at first a white precipitate of **silver hypophosphite**— AgH_2PO_2 , which soon becomes black, owing to the formation of metallic silver.
3. HgCl_2 in excess causes a white precipitate of mercurous chloride, Hg_2Cl_2 ; this takes place more rapidly on warming, and in the presence of HCl .

REACTIONS OF ORTHOPHOSPHORIC ACID (H_3PO_4).

Use a solution of sodium phosphate (Na_2HPO_4).

1. AgNO_3 causes a light yellow precipitate of **silver phosphate**— Ag_3PO_4 , soluble in HNO_3 and NH_4OH .
2. Fe_2Cl_6 in presence of sodium acetate, produces a yellowish-white, gelatinous precipitate of **ferric phosphate**— $\text{Fe}_3(\text{PO}_4)_2$. An excess of Fe_2Cl_6 must be avoided.
3. $(\text{NH}_4)_2\text{MoO}_4$ in neutral or acid solution, causes a yellow precipitate to separate slowly, which is **ammonium phosphomolybdate**— $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_9 + 2\text{H}_2\text{O}$, insoluble in HNO_3 , soluble in NH_4OH . The precipitate forms more rapidly in the presence of NH_4NO_3 .
4. Magnesia mixture (consisting of $\text{MgSO}_4, \text{NH}_4\text{Cl}, \text{NH}_4\text{OH}$) causes a white precipitate of **ammonium magnesium phosphate**— $\text{MgNH}_4\text{PO}_4 + 6\text{H}_2\text{O}$. Agitation facilitates the formation of this precipitate.
5. BaCl_2 in neutral solution, produces a white precipitate of **barium hydrogen phosphate**— BaHPO_4 .
6. Albumen (white of egg) does not cause a precipitate.

REACTIONS OF PYROPHOSPHORIC ACID ($\text{H}_4\text{P}_2\text{O}_7$).

Use a solution of sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$).

1. AgNO_3 precipitates white **silver pyrophosphate**— $\text{Ag}_3\text{P}_2\text{O}_7$, soluble in HNO_3 and NH_4OH .
2. MgSO_4 causes a white precipitate of **magnesium pyrophosphate**— $\text{Mg}_2\text{P}_2\text{O}_7$, soluble in excess of the reagent; from this solution a mixture of NH_4OH and NH_4Cl does not reprecipitate it in the cold. This reaction may be used to distinguish ortho- from pyrophosphoric acid.

3. Neither $(\text{NH}_4)_2\text{MoO}_4$, nor albumen produces a precipitate.
4. BaCl_2 , in neutral solution, precipitates white **barium pyrophosphate**— $\text{Ba}_2\text{P}_2\text{O}_7$.

REACTIONS OF METAPHOSPHORIC ACID (HPO_3).

Use a solution of sodium metaphosphate (NaPO_3).

1. AgNO_3 produces a white precipitate of **silver metaphosphate**— AgPO_3 , soluble in HNO_3 and NH_4OH .
2. Albumen forms a white precipitate with the free acid, and with the salts on the addition of acetic acid. This is an important distinction from the ortho- and pyro-acids.
3. Neither $(\text{NH}_4)_2\text{MoO}_4$ nor magnesia mixture produces a precipitate; should one form with the latter reagent, it is readily soluble in NH_4Cl .
4. BaCl_2 forms a white precipitate of **barium metaphosphate**— $\text{Ba}(\text{PO}_3)_2$.
5. Solutions of the meta- and pyro-acids in water are converted into the ortho-acid by boiling.

REACTIONS OF BORIC ACID (H_3BO_3).

Use a solution of sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$).

1. AgNO_3 produces a white precipitate of **silver borate**, soluble in HNO_3 .
2. BaCl_2 precipitates white **barium borate**, soluble in excess of water and in NH_4Cl .
3. H_2SO_4 or HCl causes the separation of the acid H_3BO_3 , in crystalline form, from strong solutions.
4. Alcohol added to the acid, and ignited, burns with a characteristic green flame. In the case of salts, the addition of alcohol is preceded by that of a few drops of H_2SO_4 , in order to liberate the free acid. This test is most successful when the acid and alcohol are added to the dry salt and not to the solution. Salts of copper when present should be removed before this test is applied, as they likewise impart a green color to the alcohol flame.

REACTIONS OF CARBONIC ACID (H_2CO_3).

Use a solution of sodium carbonate (Na_2CO_3).

1. All free acids except HCN and H_2S decompose carbonates with effervescence. The escaping gas passed into a solution of $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$ causes a white precipitate.
2. BaCl_2 , in neutral solution precipitates white **barium carbonate**— BaCO_3 , soluble in acids.
3. CaCl_2 precipitates white **calcium carbonate**— CaCO_3 , soluble in acids with effervescence.

REACTIONS OF SILICIC ACID (H_4SiO_4).

Use a solution of sodium silicate, (Na_4SiO_4).

1. Insoluble silicates are determined by fusing on platinum foil some of the fine powder with Na_2CO_3 , treating the fused mass with H_2O and HCl , evaporating to dryness and redissolving in H_2O , when the silica, SiO_2 will remain as a fine white precipitate.
2. Before the blowpipe, with a bead of microcosmic salt, silica forms the so-called *silica skeleton*, which is very characteristic.
3. Soluble silicates give gelatinous precipitates of **silicic acid**— H_4SiO_4 , on the addition of H_2SO_4 or HCl ; on evaporating this to dryness with a little HCl , and redissolving in H_2O , *silica*— SiO_2 , remains.
4. NH_4Cl also precipitates H_4SiO_4 when added to a soluble silicate.

REACTIONS OF HYDROFERROCYANIC AND
HYDROFERRICYANIC ACIDS.

These acids have been sufficiently characterized under iron.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP II.

I. Try the solution with litmus paper; if alkaline, hydrates, carbonates, borates, silicates and, possibly, phosphates, may be present. If the solution is acid, neutralize with NaOH before applying the following tests :—

II. Evaporate a portion of the solution to dryness, and add concentrated H_2SO_4 . The following acids will give characteristic reactions, and may be recognized by the further application of tests previously given :—

HClO and HClO_3 give the odor of chlorine. They are readily distinguished by the chlorate deflagrating with charcoal, by its liberating oxygen on heating, and by the yellowish-green gas, Cl_2O_4 , which is given off. The addition of H_2SO_4 to a chlorate should be performed with very small quantities and with great care, on account of the tendency of the chlorine tetroxide to decompose with explosive violence. The most characteristic difference of HClO is the white precipitate of AgCl which it gives with AgNO_3 .

H_2S is recognized by its peculiar odor, and by blackening a piece of filter paper moistened with solution of lead acetate.

H_2SO_3 and $\text{H}_2\text{S}_2\text{O}_3$ give off SO_2 , readily recognized by its odor and bleaching property. They are distinguished from each other by H_2SO_4 producing with a concentrated solution of thiosulphate a white precipitate of sulphur in addition to the liberation of SO_2 .

HNO_3 is detected by the peculiar acid fumes, which become red when metallic copper is added with the H_2SO_4 . All the special tests, previously given, of this acid should be applied before a conclusion is reached concerning the presence or absence of it.

HH_2PO_3 is readily detected by its odor.

H_3BO_3 is easily detected when, in addition to the H_2SO_4 , some alcohol is added and ignited. In the absence of salts of copper, the green flame is evidence of this acid. *This green flame will show best when the acid and alcohol are added to the dry salt.*

H_2CO_3 is recognized by effervescence *with the dilute acid in the cold* without odor. This test should be applied to the original solution, using preferably acetic acid. When other gases are given off at the same time, the CO_2 may be detected by passing into lime water, which will cause a precipitate of CaCO_3 .

H_4SiO_4 is precipitated as a white, gelatinous mass when the H_2SO_4 is added to a soluble silicate. Insoluble silicates will be treated of later.

$\text{H}_4\text{Fe}(\text{CN})_6$ and $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ give the odor of HCN . Their presence is confirmed by the use of FeSO_4 and Fe_2Cl_6 .

III. The acids of this group not detected by H_2SO_4 are sulphuric and the three phosphoric acids.

H_2SO_4 is precipitated, on the addition of BaCl_2 , as BaSO_4 , insoluble in HCl or HNO_3 .

H_3PO_4 is precipitated yellow on the addition of AgNO_3 , the precipitate being soluble in HNO_3 (distinction from HCl , HBr and HI). $(\text{NH}_4)_2\text{MoO}_4$ is the most distinctive test. It causes a yellow precipitate when a few drops of the solution are added to some of the reagent in a test tube and warmed gently (distinction from $\text{H}_4\text{P}_2\text{O}_7$ and HPO_3). Magnesia mixture is also a characteristic test for this acid.

$\text{H}_4\text{P}_2\text{O}_7$ gives a white precipitate with AgNO_3 . It is further distinguished from the ortho-acid by $(\text{NH}_4)_2\text{MoO}_4$, and from the meta-acid by its behavior with MgSO_4 , and with albumen. HPO_3 also gives a white precipitate with AgNO_3 . It is best distinguished from the other varieties by albumen, by negative tests, and by boiling for some time and then applying the tests for the ortho-acid.

H_3AsO_4 and H_2CrO_4 might be classified with this group, but a little care on the part of the student will detect them among the bases, and a little thought will tell him how to prove whether they are present as acids or bases.

GROUP III.

ACETIC ACID.		TARTARIC ACID.	
VALERIANIC ACID.		CITRIC	"
STEARIC	"	CARBOLIC	"
OLEIC	"	BENZOIC	"
LACTIC	"	SALICYLIC	"
OXALIC	"	GALLIC	"
SUCCINIC	"	TANNIC	"
MALIC	"		

REACTIONS OF ACETIC ACID ($\text{HC}_2\text{H}_3\text{O}_2$).

Use a solution of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$).

1. In the free state acetic acid is readily recognized by its odor.
2. H_2SO_4 , added to an acetate and the mixture warmed, gives the characteristic odor.
3. H_2SO_4 and $\text{C}_2\text{H}_5\text{OH}$ in equal volumes added to an acetate form **acetic ether**, readily recognized by its odor.
4. Fe_2Cl_6 , with a neutral acetate, forms a deep red color, due to **ferric acetate**— $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$.

VALERIANIC ACID ($\text{HC}_6\text{H}_9\text{O}_2$).

The odor is sufficient evidence of the presence of this acid. This odor is developed by moisture and heat, and in the case of the salts by the addition of H_2SO_4 .

STEARIC ACID ($\text{HC}_{18}\text{H}_{35}\text{O}_2$).

Stearic acid is a white, fatty solid, melting at 69.2°C ., giving when combined with potassium a soft soap, and with sodium a hard soap; from both it separates as an oily liquid on the addition of HCl , becoming solid on cooling. The lead salt, lead stearate, $\text{Pb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$, is insoluble in ether.

OLEIC ACID ($\text{HC}_{18}\text{H}_{33}\text{O}_2$).

Oleic acid is an oily liquid at ordinary temperatures, but becomes solid at 4°C . and remains so until the temperature rises to 14°C ., when it again becomes liquid. Lead Oleate— $\text{Pb}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$, prepared by saturating sodium oleate with acetic acid and adding lead acetate, is almost entirely soluble in ether. This is an important distinction from stearic acid.

LACTIC ACID ($\text{HC}_3\text{H}_5\text{O}_3$).

Lactic acid is a colorless, syrupy liquid, of a slight unpleasant odor and a very sour taste, soluble in water, alcohol and ether, but insoluble in chloroform. When heated with H_2SO_4 , CO is evolved. Lactates are all soluble in water, most of them sparingly; they are insoluble in ether.

$\text{Hg}_2(\text{NO}_3)_2$ boiled with strong solution of a lactate, deposits crimson mercurous lactate— $\text{Hg}_2(\text{C}_3\text{H}_5\text{O}_3)_2$.

REACTIONS OF OXALIC ACID ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$).

Use a solution of ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$).

1. $\text{K}_2\text{Mn}_2\text{O}_8$, acidulated with H_2SO_4 , is decolorized.
2. BaCl_2 produces a white precipitate of **barium oxalate**— BaC_2O_4 , sparingly soluble in acetic or oxalic acid, and freely soluble in HCl , HNO_3 and NH_4Cl .
3. AgNO_3 precipitates white **silver oxalate**— $\text{Ag}_2\text{C}_2\text{O}_4$, readily soluble in hot concentrated HNO_3 , sparingly so in dilute acid, soluble in NH_4OH .
4. CaCl_2 produces, even in highly dilute solutions, a white precipitate of **calcium oxalate**— CaC_2O_4 , soluble in HCl and HNO_3 , but insoluble in acetic acid.
5. FeSO_4 with dilute solutions causes a yellow color; with more concentrated solutions and warming, a yellow precipitate **ferrous oxalate**— FeC_2O_4 , falls. This precipitate is insoluble in acetic acid, but is dissolved by HCl and HNO_3 .

SUCCINIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_4$).

Use a solution of sodium succinate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_4$).

1. BaCl_2 produces no precipitate, but on the addition of alcohol a white precipitate of **barium succinate**— $\text{BaC}_4\text{H}_4\text{O}_4$, falls, soluble in NH_4Cl .
2. Fe_2Cl_6 causes a brownish-red, bulky precipitate of **ferric succinate**— $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_4)_3$.
3. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates white amorphous **lead succinate**— $\text{PbC}_4\text{H}_4\text{O}_4$, soluble in HNO_3 .

MALIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$).

1. CaCl_2 fails to give a precipitate with the acid or its salts, until the mixture is boiled, when **calcium malate**— $\text{CaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, separates. The addition of alcohol will cause this precipitate without boiling.

2. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ precipitates white **lead malate**— $\text{PbC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$.

REACTIONS OF TARTARIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$).

Use a solution of sodium tartrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$).

1. BaCl_2 precipitates white **barium tartrate**— $\text{BaC}_4\text{H}_4\text{O}_6$, soluble in ammonium salts, and in HCl .
2. CaCl_2 produces a white precipitate of **calcium tartrate**— $\text{CaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, ammonium salts prevent this precipitation. On adding KOH to this precipitate, it dissolves; boil this solution, calcium tartrate is again precipitated. Acetic acid is also a solvent for this precipitate.

3. AgNO_3 causes a white precipitate of **silver tartrate**— $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$; on adding a few drops of NH_4OH to dissolve the precipitate, and boiling, a mirror of metallic silver forms on the test tube. The test tube must be perfectly cleaned for this reaction; to accomplish this, rinse the tube with KOH solution and then thoroughly with water.

4. $\text{Ca}(\text{OH})_2$ in excess causes a precipitate of **calcium tartrate**— $\text{CaC}_4\text{H}_4\text{O}_6$. This precipitate is flocculent at first, in which state it is readily soluble in NH_4Cl , but after standing for some time it becomes crystalline, in which case it is insoluble in NH_4Cl .

5. Tartaric acid and tartrates char on heating, and with H_2SO_4 the odor of burnt sugar is given off.

REACTIONS OF CITRIC ACID ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$).

Use a solution of sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$).

1. BaCl_2 produces a white precipitate of **barium citrate**— $\text{Ba}_3(\text{C}_6\text{H}_5\text{O}_7)_2$, soluble in excess of water, in ammonium salts, and in acids.

2. CaCl_2 precipitates white **calcium citrate**— $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ more insoluble in hot than in cold water, soluble in cold NH_4Cl , but insoluble in KOH .

3. AgNO_3 produces a white precipitate of **silver citrate**— $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$; on boiling no metallic mirror is formed.

4. $\text{Ca}(\text{OH})_2$, in excess, does not cause a precipitate until the mixture is boiled. This is an important distinction from tartaric acid.

5. Citric acid and citrates char on heating, and with H_2SO_4 give off the odor of burnt sugar.

CARBOLIC ACID ($\text{C}_6\text{H}_5\text{OH}$).

1. HNO_3 , with an aqueous solution of the acid, forms a yellow color, due to formation of **picric acid**— $\text{C}_6\text{H}_2(\text{NO}_3)_3\text{OH}$

2. Fe_2Cl_6 produces a violet blue color.

3. A piece of pine wood dipped in the acid, and then exposed to the fumes of HCl , becomes after a short time colored blue.

4. Bromine water causes a white flocculent precipitate.

5. Albumen is coagulated by the free acid.

BENZOIC ACID ($\text{HC}_7\text{H}_5\text{O}_2$).

1. Fe_2Cl_6 precipitates from neutral solutions, flesh-colored **ferric benzoate**— $\text{Fe}_2(\text{C}_7\text{H}_5\text{O}_2)_6$, soluble in HCl, with separation of benzoic acid.
2. HCl causes the separation of benzoic acid from cold solutions of the benzoates.
3. BaCl_2 and CaCl_2 produce no precipitates with either the free acid or its salts.
4. Benzoic acid is *readily soluble* in petroleum ether.
5. The pure acid melts at 121.4°C .

SALICYLIC ACID ($\text{HC}_7\text{H}_5\text{O}_3$).

1. Fe_2Cl_6 produces a deep violet color, which is very characteristic.
2. Warmed with H_2SO_4 and methyl alcohol, the fragrant odor of methyl salicylate (oil of wintergreen) is developed.
3. HCl causes the separation of the free acid from cold solutions of the salicylates.
4. Salicylic acid is *insoluble* in petroleum ether; this fact enables one to separate mixtures of benzoic and salicylic acids.
5. The pure acid melts at 155.5°C .

GALLIC ACID ($\text{HC}_7\text{H}_5\text{O}_6 \cdot \text{H}_2\text{O}$).

1. FeSO_4 produces no change.
2. Fe_2Cl_6 produces a bluish-black precipitate, which disappears on heating.
3. KOH, if not in excess, develops slowly a deep green color, which becomes red on the addition of acids. Alkaline carbonates cause the same green color, although more slowly.
4. No precipitate is produced with either gelatin or the alkaloids. With the former, however, a precipitation takes place when gum is present.

TANNIC ACID ($\text{C}_{14}\text{H}_{10}\text{O}_9$).

1. FeSO_4 , when perfectly pure, causes no change; in the presence of oxygen, however, a dark color rapidly develops, which on standing, slowly becomes a precipitate.

2. Fe_2Cl_6 produces a bluish-black precipitate.
3. Normal solution of iodine mixed with a small quantity of ammonia, previously diluted with ten times its volume of water, produces a brilliant red color. This reaction will take place with only traces of tannin.
4. Gelatin causes a white flocculent precipitate. This reaction is more delicate in the presence of small quantities of alum.
5. Alkaloids produce white precipitates, soluble in acetic acid and alcohol.
6. $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ causes a white, gelatinous precipitate. Most metallic salts cause precipitates with tannin.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP III.

As many of the acids in this group would indicate their presence by odor or physical appearance, a method of separating only the more important and closely related ones will be given. The list will therefore be limited to Acetic acid, Oxalic acid, Tartaric acid and Citric acid.

If the solution is Acid to Litmus Paper, neutralize with NaOH.

I. To a small portion add H_2SO_4 and warm. Acetic acid will, if present, be detected by its odor.

II. To another portion add NH_4OH until slightly alkaline, and then CaCl_2 ; allow to stand (avoiding heat) for ten minutes, and filter.

Ppt. $\text{H}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_4\text{H}_2\text{O}_6$. Wash, pour on the filter $\text{HC}_2\text{H}_3\text{O}_3$.		Filt. $\text{H}_2\text{C}_2\text{H}_3\text{O}_3$. Boil to remove NH_4OH , a white ppt. slowly forms on sides of the tube.
Ppt. $\text{H}_2\text{C}_2\text{O}_4$. Confirm by testing original solution with $\text{HC}_2\text{H}_3\text{O}_3$ and CaCl_2 .	Filt. $\text{H}_2\text{C}_4\text{H}_2\text{O}_6$. Add NH_4OH until slightly alkaline, white ppt. Confirm by forming mirror with AgNO_3 in original solution.	

SECTION III.

DETECTION OF BASES AND ACIDS.

SPECIAL OBSERVATION.

The bases must always be determined first in a portion of the solution or powder, according to chart, page 67.

If only the alkali metals are present and the reaction is neutral, proceed to search for the acids according to DIVISION I.

If other than the alkali metals are present and the reaction is acid, proceed to search for the acids according to DIVISION II.

When the substance is not entirely dissolved by H_2O , HCl , or a mixture of HCl and HNO_3 , proceed for both bases and acids according to DIVISION III.

It will be seen from the above that before beginning the analysis of a solution it is necessary to try its action on litmus paper. If the reaction is alkaline it is necessary to neutralize with HCl , bearing in mind the precautions on page 68.

When the analysis of a solid is to be performed, the action on litmus paper of the portion soluble in water is also to be noted, and the solution made neutral if necessary.

All the physical properties of the solid should be carefully observed.

Certain acids, when present, like benzoates and salicylates, are precipitated by HCl , in which case it would first be necessary to evaporate to dryness and heat to redness.

EXCEPTION IN SEARCHING FOR BASES.

When phosphates are present in acid solution, determined by adding a few drops of the solution to some HNO_3 and $(NH_4)_2MoO_4$ and warming gently, the following chart must be used in the separation of Group IV. That is, bring the precipitate containing Fe , Ce , Al , Cr , from chart, page 67, and work according to this. Oxalates also cause an exception

to the general chart for separation of bases ; when, therefore, their presence is suspected, heat the substance to redness before examining for bases.

DIRECTIONS FOR THE ANALYSIS OF GROUP IV WHEN PHOSPHATES ARE PRESENT.

In addition to Fe, Ce, Al, Cr, there may be present the phosphates of Ca, Sr, Ba, Mn, Mg. Dissolve the precipitate in HCl, add Na_2HPO_4 in excess, then excess of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$; boil, filter.

Ppt. $\text{Fe}_2(\text{PO}_4)_3$, $\text{Al}_2(\text{PO}_4)_3$, $\text{Ce}_2(\text{PO}_4)_3$. Wash with hot H_2O , then pour on the filter hot solution KOH.		Filt. Ba, Sr, Ca, Mn, Mg, Cr. (If green Cr is present) Add K_2CrO_6 , warm, filter.	
Ppt. Fe, Ce. Wash, dissolve in HCl and test a portion with $\text{K}_4\text{Fe}(\text{CN})_6$ for Fe	Filt. $\text{Al}_2(\text{PO}_4)_3$ Acidify with $\text{HC}_2\text{H}_3\text{O}_2$ white ppt = Al.	Ppt. Ba Yellow.	Filt. Sr, Ca, Mn, Mg Add very dilute H_2SO_4 allow to stand, filter. An excess of H_2SO_4 should be avoided.
		Ppt. Sr. Confirm by flame test.	Filt. Ca, Mn, Mg Add $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, filter.
To another portion add $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$, then NH_4OH in excess and Na_2HPO_4 , white precipitate = Ce		Ppt. Ca. White	Filt. Mg, Mn. Evaporate a portion to dryness and test with borax bead for Mn. To the remaining portion add Fe_2Cl_6 , filter out the $\text{Fe}_2(\text{PO}_4)_3$, to filtrate add NH_4Cl , NH_4OH and NH_4HS , to separate Fe and Mn, filter and test filtrate with Na_2HPO_4 , white ppt. = Mg.

DIVISION I.—When the bases are the alkali metals, and the reaction is neutral.

RULE I.—*Evaporate a portion of the solution to dryness, and slowly heat to redness.*

If the mass chars, one or more of the following *organic acids* are indicated: ACETATES, TARTRATES, CITRATES, GALLATES, TANNATES.

NOTE.—Oxalates do not char, although if the heating take place slowly a grayish coloration may be noticed, the residue in this case giving off CO_2 on the addition of H_2SO_4 .

Fe_2Cl_6 immediately detects TANNATES and GALLATES. Gallic acid crystallizes in the cold on acidifying the solution. Tannic acid precipitates with solution of gelatin. The other organic acids are separated and detected according to chart, page 86.

RULE II.—*Add to a second portion of the concentrated solution, or the dry salt, strong H_2SO_4 , warm gently, and note any of the following effects:—*

Effervescence with <i>dilute</i> acid in the cold, no odor,	} Carbonates.
Effervescence on heating, no odor, . . .	
Effervescence with dilute acid on heating, odor of H_2S ,	} Oxalates, confirm by $CaCl_2$ and $HCl_3H_3O_3$.
Odor of SO_2 ,	
Odor of SO_2 with precipitation of S , . . .	} Sulphides.
Dark brown color and violet fumes, . . .	
Dark red color and reddish fumes, . . .	} Sulphites.
Odor of HCN ,	
Odor of HCN with crystalline deposit, . .	} Thiosulphates.
Odor of acetic acid,	
With dilute acid, odor of chlorine, . . .	} Iodides, confirm by starch and Cl water.
With strong acid, odor of chlorine, . . .	
Strongly acid suffocating fumes,	} Bromides, confirm by starch and Cl water.
Strongly acid fumes, becoming red when metallic Cu is added,	
Characteristic odors,	} Cyanides.
	} Ferro- or Ferri-cyanides, confirm by Fe_2Cl_6 and $FeSO_4$.
	} Acetates.
	} Hypochlorites.
	} Chlorates.
	} Chlorides, confirm by $AgNO_3$.
	} Nitrates, confirm by $FeSO_4$ and H_2SO_4 , also by indigo solution.
	} Benzoates, Succinates, Valerianates, Carbolates, Hypophosphites.

RULE III.—*To a third portion add $BaCl_2$.*

A white precipitate insoluble in HCl indicates SULPHATES.

RULE IV.—*To a fourth portion add $CaCl_2$.*

A white precipitate soluble in excess of H_2O indicates SULPHATES; if insoluble in excess of H_2O and in acetic acid, OXALATES are indicated. A white precipitate soluble in KOH , reprecipitated on boiling, indicates TARTRATES; confirm by boiling with NH_4OH and $AgNO_3$, forming a mirror of silver on the test tube.

A white precipitate soluble in NH_4Cl and reprecipitated on boiling, indicates CITRATES. Citrates and Tartrates are also detected by heating some of the dry salt with H_2SO_4 , when the odor of burnt sugar is developed.

When all four of these acids are suspected to be present, treat the solution with HCl and $BaCl_2$ to remove sulphates;

then neutralize the excess of HCl with NaOH, and proceed according to chart, page 86.

RULE V.—*To a fifth portion, acidified with HNO_3 , add AgNO_3 .*

A white, curdy precipitate, immediately and completely soluble in NH_4OH , indicates CHLORIDES. If slowly soluble in NH_4OH , BROMIDES may be present; confirm by chlorine water and starch.

A yellowish precipitate insoluble in NH_4OH = IODIDES. A white precipitate soluble in strong, hot HNO_3 = CYANIDES. When bromides and iodides are present, they may be separated by adding to the original solution chlorine water and starch; continue the addition of chlorine water until the blue color of the starch iodide is discharged, then shake with chloroform; when a yellowish-red color is imparted to the separated chloroform, Br is indicated.

For further instruction regarding the separation of these acids, consult chart, page 72.

RULE VI.—*Add to a sixth portion of the solution Magnesia Mixture.*

A white precipitate indicates PHOSPHATES and ARSENATES. In another portion separate the As by HCl and H_2S , and repeat the test for H_3PO_4 in the filtrate by neutralizing and adding magnesia mixture.

RULE VII.—*To a seventh portion add Fe_2Cl_6 .*

This reagent readily indicates TANNATES, GALLATES, FERRO- and FERRI-CYANIDES.

RULE VIII.—*To an eighth portion apply the special test with H_2SO_4 and FeSO_4 for NITRATES.*

RULE IX.—*To a ninth portion of the dry salt, or the solution evaporated to dryness, add a few drops of strong H_2SO_4 and 15 to 20 drops of alcohol, mix well and apply flame. BORATES, if present, will impart a green color to the flame.*

DIVISION II.—When the solution is acid, or, if a solid, requires the use of HCl to dissolve it.

After determining the bases, bearing in mind the exception in regard to phosphates, a portion of the substance is tested according to Rules I and II, DIVISION I.

A second portion is treated as follows :—

Boil with strong solution Na_2CO_3 , filter.

Ppt. consists of the carbonates, hydrates, and oxides of the bases present, and is disregarded.	Filt. contains the acids in combination with Na. Divide in two parts.	
	First portion. Add HCl until slightly acid, boil to remove CO_2 , neutralize with NaOH, and test according to Rules III, IV, VI, VII, VIII and IX, DIVISION I.	Second portion. Add HNO_3 until slightly acid, boil to remove CO_2 , neutralize with NaOH, and test according to Rule V, and if necessary, III, IV, VI, VII and IX, DIVISION I.

DIVISION III.—When the substance is not entirely dissolved by H_2O , HCl, or a mixture of HCl and HNO_3 .

Add water and filter; the filtrate, if it contains solid matter, is examined for bases by chart, page 67, and for acids by Division I. The residue, after treatment with water, is treated with HCl, or if necessary, with a mixture of HCl and HNO_3 , and, if it contain any solid matter, examined for bases by chart, page 67, and for acids according to Division II. The insoluble residue consists of one or more of the following substances: Sulphates of Ba, Sr, Ca, Pb; Chlorides, Bromides and Iodides of Ag, Pb; certain Oxides which have been highly heated, as Fe_2O_3 , Al_2O_3 , Cr_2O_3 and SnO_2 ; Silica and Silicates; Carbon and Sulphur (the last two are readily detected in the preliminary examination by heat). This insoluble residue is mixed with about four times its weight of dry sodium carbonate and fused on a platinum foil; the mass is boiled with water, and the soluble portion examined for bases by chart, page 67, and for acids according to Division I. The insoluble portion is treated with HCl, evaporated to dryness, redissolved in water with a little HCl, and examined, after determining the bases, according to Division II. Any insoluble substance remaining is probably silica, which may be determined by a bead of salt of phosphorus before the blow-

pipe, showing the skeleton of silica. If the metals lead and silver are present in this insoluble residue, they are best determined by treating the residue insoluble in HCl , by HNO_3 and examining according to Division II. Many of these insoluble substances are detected in a preliminary examination by the use of the blowpipe, as explained in the tests given under the individual elements.

The following chart, taken largely from Dr. Mütter's Analytical Chemistry, will be found useful to consult after determining the bases and before commencing the examination for acids.

Bases found.	If soluble in water, test for the following acids	If insoluble in water, but soluble in acids, test for the following acids	If insoluble in acids, fuse with Na_2CO_3 and test for,
Ag,	$\text{HNO}_3, \text{HNO}_2, \text{H}_2\text{SO}_4, \text{HC}_2\text{H}_3\text{O}_2,$	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4, \text{HCN}, \text{H}_2\text{C}_2\text{O}_4, \text{H}_2\text{C}_4\text{H}_4\text{O}_6, \text{H}_2\text{C}_6\text{H}_8\text{O}_7,$	Cl, I, Br.
Hg(ous),	$\text{HNO}_3, \text{HC}_2\text{H}_3\text{O}_2, \text{H}_2\text{SO}_4,$	Oxide, Sulphide, Cl, I, Oxysulphate.	Cl, I, Br.
Hg(ic),	Cl, $\text{HNO}_3, \text{H}_2\text{SO}_4, \text{HC}_2\text{H}_3\text{O}_2,$	Oxide, Sulphide, I, Oxysulphate	Sulphide, Iodide.
Pb,	$\text{HC}_2\text{H}_3\text{O}_2, \text{HNO}_3,$	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4, \text{H}_2\text{C}_2\text{O}_4,$	$\text{H}_2\text{SO}_4, \text{Cl}, \text{I}, \text{H}_2\text{CrO}_4,$
Bi,	$\text{HNO}_3, \text{Cl}, \text{H}_2\text{SO}_4, \text{HC}_2\text{H}_3\text{O}_2, \text{H}_2\text{C}_6\text{H}_8\text{O}_7,$	Oxynitrate, Oxychloride, Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4,$	None.
Cu(ic),	Cl, $\text{HNO}_3, \text{H}_2\text{SO}_4, \text{HC}_2\text{H}_3\text{O}_2,$	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4, \text{Oxyacetate}.$	"
Cu(ous),	$\text{H}_2\text{SO}_4,$	Oxide, I.	"
Cd,	Cl, $\text{HNO}_3, \text{I}, \text{H}_2\text{SO}_4,$	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4,$	"
Sb,	$\text{Cl}, \text{H}_2\text{C}_4\text{H}_4\text{O}_6,$	Oxide, Sulphide, Oxychloride.	"
Sn(ic),	Cl,	Oxide.	"
Sn(ous),	Cl, $\text{H}_2\text{SO}_4,$	Oxide, Sulphide, $\text{H}_3\text{PO}_4, \text{H}_2\text{CrO}_4,$	"
Au,	Cl,	Sulphide.	"
Pt,	Cl,	Sulphide.	"
Fe(ic),	Cl, $\text{HNO}_3, \text{H}_2\text{SO}_4, \text{HC}_2\text{H}_3\text{O}_2,$	Oxide, Sulphide, I, $\text{H}_3\text{PO}_4,$	"
Fe(ous),	Cl, $\text{H}_2\text{SO}_4, \text{I},$	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4,$	"
Al,	Like Iron,	Oxide, $\text{H}_3\text{PO}_4,$	"
Ce,	Cl,	Oxide, $\text{H}_2\text{C}_2\text{O}_4,$	Oxide.
Cr,	Cl, $\text{H}_2\text{SO}_4, \text{HC}_2\text{H}_3\text{O}_2, \text{HNO}_3,$	Oxide, $\text{H}_3\text{PO}_4,$	Oxide
Mn,	Like Chromium,	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4,$	None.
Zn,	Like Chromium,	Like Manganese.	"
Co,	Cl, $\text{HNO}_3, \text{H}_2\text{SO}_4,$	Oxide, Sulphide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4,$	"
Ni,	Like Cobalt,	Like Cobalt	"
Ba,	Cl, $\text{HNO}_3, \text{HC}_2\text{H}_3\text{O}_2,$	$\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4, \text{H}_2\text{C}_2\text{O}_4, \text{H}_2\text{CrO}_4,$	Sulphate.
Sr,	Like Barium,	Like Barium.	"
Ca,	Like Barium,	Like Barium.	Sulphate.
Mg,	Cl, $\text{H}_2\text{SO}_4,$	Oxide, $\text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4,$	None
Li,	All Radicals,	$\text{H}_3\text{PO}_4,$	"
K,	All Radicals,	$\text{K}_2\text{PtCl}_6, \text{KHC}_4\text{H}_4\text{O}_6,$	"
Na,	All Radicals,	None.	"
$\text{NH}_4,$	All Radicals,	None	"

SECTION IV.

SOME OF THE REACTIONS AND TESTS OF PURITY OF THE
MORE IMPORTANT ORGANIC COMPOUNDS.

CHLOROFORM (CHCl_3).

"A heavy, clear, colorless, diffusive liquid, of a characteristic, pleasant, ethereal odor, a burning, sweet taste, and a neutral reaction."

1. Agitate about 5 c.c. with twice its volume of distilled water, separate and test the aqueous portion with litmus paper; no change should be produced, showing the absence of acids. To a small portion of the water add AgNO_3 ; a white precipitate would indicate HCl , the result of decomposition. To another portion add solution of KI ; a reddish color would indicate *Chlorine*. Another portion warmed with solution KOH should not become colored, showing the absence of aldehyde.

2. 10 c.c. of chloroform mixed with half its volume of strong H_2SO_4 , and, after agitation, set aside, should not cause a color in either liquid for twenty-four hours.

3. H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, mixed with an equal volume of chloroform and warmed, will become green, indicating the presence of a small quantity of *alcohol*.

IODOFORM (CHI_3).

Iodoform occurs in small, lemon-yellow, lustrous crystals, having a saffron-like odor, and an unpleasant, slightly sweetish, iodine-like taste. Its solutions have a neutral reaction.

1. Digest a small quantity of iodoform with alcoholic solution of KOH , acidify with dilute HNO_3 , and add starch paste, when the blue color of starch iodide will be developed.

2. Agitate a small quantity of iodide with distilled water and filter; the filtrate should not affect litmus paper. Add to a portion of the filtrate AgNO_3 ; a yellowish precipitate would indicate iodides as an impurity. Evaporate another small

portion to dryness; no residue should remain, indicating the absence of soluble impurities.

ALCOHOL (C_2H_5OH).

"A transparent, colorless, mobile and volatile liquid, of a characteristic, pungent and agreeable odor, and a burning taste. It should not change the color of blue litmus paper, previously moistened with water. It boils at 78° C. and is readily inflammable, giving a blue flame without smoke."

1. Add to 5 c. c. of alcohol in a test tube an equal volume of H_2SO_4 to which has been added a small quantity of $K_2Cr_2O_7$, and warm; the odor of aldehyde will be developed, the liquid in the tube becoming green.

2. On heating 10 c. c. of alcohol with about one-fourth its volume of H_2SO_4 the odor of ether will be evolved.

3. Equal volumes of H_2SO_4 , acetic acid and alcohol, on warming, will give the odor of acetic ether. If much amyl alcohol be present the odor of amyl acetate may also be recognized.

4. Evaporate 10 c. c. of alcohol to about one-fifth its bulk, and add an equal volume of strong sulphuric acid; a reddish color will indicate amyl alcohol.

5. Mix in a test tube 5 c. c. of alcohol with an equal volume of solution KOH; an immediate darkening will indicate the presence of methyl alcohol, aldehyde or oak tannin.

CHLORAL HYDRATE ($C_2Cl_3OH \cdot H_2O$).

(*Chloral*, U. S. P.)

Chloral hydrate occurs in colorless, transparent crystals, slowly vaporizing on exposure to the air, having an aromatic, penetrating and slightly acrid odor, bitterish, caustic taste and a neutral reaction. It liquefies when mixed with carbolic acid or with camphor.

1. In a test tube heat to boiling a small quantity of chloral hydrate and water and add solution KOH; a vaporous milky mixture of chloroform results, readily recognized by its odor, while formate of potassium remains in solution.

2. To a hot aqueous solution of chloral hydrate in a test

tube, add AgNO_3 , then NH_4OH and boil; a silver mirror is deposited on the tube.

3. To another portion of an aqueous solution add a few drops of HNO_3 and AgNO_3 ; no precipitate should be produced, indicating the absence of HCl .

4. Add NH_4HS to an aqueous solution; a reddish-brown coloration results, which on standing deposits a reddish-brown compound mixed with sulphur.

5. A crystal of chloral hydrate heated on platinum foil should volatilize without residue.

GLYCERIN ($\text{C}_3\text{H}_8(\text{OH})_3$).

"A clear, colorless liquid, of a syrupy consistence, oily to the touch, hygroscopic, without odor, very sweet and slightly warm to the taste, and neutral in reaction."

1. Make a borax bead in the loop of a platinum wire, moisten it with a small quantity of glycerin (previously rendered alkaline with a dilute solution of soda), and hold in the colorless flame of a Bunsen burner; the flame is tinged green, owing to the liberation of boric oxide.

2. Warm 5 c.c. of glycerin with an equal volume of H_2SO_4 ; no coloration should result, showing the absence of cane sugar.

3. Heat a few drops on platinum foil; no residue should be left.

4. A portion heated nearly to the boiling point with an equal volume of Fehling's solution, should not deposit a red precipitate of cuprous oxide, Cu_2O . The same result should be obtained if the glycerin be previously boiled with a small quantity of HCl , showing the absence of sugars, starch and dextrin.

GLUCOSE ($\text{C}_6\text{H}_{12}\text{O}_6$).

(*Dextrose, Grape Sugar.*)

1. To a dilute solution of glucose, add an equal volume of Fehling's solution and boil; a red precipitate of cuprous oxide, Cu_2O , is deposited.

2. A strong solution mixed with H_2SO_4 , in the cold; no change should occur; if, however, organic impurities are present, a dark coloration will result.

3. To a strong solution of glucose add a solution of KOH and warm; the solution becomes yellow and, finally, brown.

SACCHAROSE ($C_{12}H_{22}O_{11}$).

(*Cane Sugar*.)

1. Boil a moderately dilute solution of sugar with a few drops of HCl, neutralize and add Fehling's solution; red cuprous oxide, Cu_2O , will be precipitated. If the sugar be pure this reaction will not take place unless it be previously boiled with the acid.

2. To a cold saturated solution add an equal volume of concentrated H_2SO_4 ; there is an immediate blackening and swelling until the tube is filled with a dry coke.

AMYLOSE ($C_6H_{10}O_5$)_x.

(*Starch*.)

Starch usually occurs as a fine, white powder, insoluble in cold water, soluble in boiling water forming a thick paste when cold.

1. To a cold dilute solution add potassium iodide and a few drops of chlorine water; the deep blue color of starch iodide results. This is decolorized by heating and reappears on cooling. It is bleached by excess of chlorine water.

2. Heat a small quantity of starch on platinum foil; it should char and finally disappear without residue.

3. Triturate a small quantity of starch with cold water, filter, and test the filtrate with litmus; no change should take place.

MORPHINE ($C_{17}H_{19}NO_3 \cdot H_2O$).

1. To some crystals of morphine sulphate on a crucible lid, or other white porcelain surface, add a small quantity of neutral solution of ferric chloride; a blue color is produced, which rapidly fades. The presence of free sulphuric acid must be avoided.

2. Similarly, to another portion add a drop of strong HNO_3 ; a red color at first forms, which rapidly becomes yellow.

3. To a solution of the sulphate add carefully a dilute

solution of KOH ; a white precipitate forms, which is readily soluble in excess. NH_4OH and Na_2CO_3 produce the same precipitate *insoluble* in excess.

4. A few crystals on a white porcelain surface should entirely dissolve in strong H_2SO_4 without color, becoming reddish on standing, and on the addition of a crystal of $\text{K}_2\text{Cr}_2\text{O}_7$ a greenish color is produced. A purple or violet color would indicate the presence of strychnine or brucine.

STRYCHNINE ($\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$).

1. A small quantity of the alkaloid dissolved in a drop or two of H_2SO_4 , and a small crystal of $\text{K}_2\text{Cr}_2\text{O}_7$ added will cause a deep blue color, rapidly changing to violet, then cherry-red, and finally fading.

2. Strong HNO_3 added to strychnine should not cause more than a very faint red color, showing the absence of brucine.

3. KOH added to a solution of the sulphate causes a white precipitate, insoluble in excess.

QUININE ($\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$).

1. To an aqueous solution of the sulphate add fresh chlorine water and then NH_4OH in slight excess, when a green color is formed, due to *Thalleioquin*.

2. To a very dilute, slightly acid solution, add chlorine water, then a small quantity of $\text{K}_4\text{Fe}(\text{CN})_6$, and finally a few drops of NH_4OH ; a red color is produced, which rapidly fades.

3. Add KOH to an aqueous solution of the sulphate ; a white precipitate forms, *insoluble* in excess. Under the same circumstances NH_4OH produces a white precipitate, *soluble* in excess.

CINCHONIDINE ($\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}$).

1. To an aqueous solution of the sulphate add NH_4OH ; a white precipitate forms almost insoluble in excess.

2. $\text{KNaC}_4\text{H}_4\text{O}_6$ added to a neutral solution produces a white precipitate.

3. To a cold saturated solution of the sulphate add $\text{KNa-C}_4\text{H}_4\text{O}_6$ in slight excess, allow to stand a short time at about 15°C. , filter and to the filtrate add a drop of NH_4OH ; not more than a slight turbidity should result, showing the absence of more than small quantities of the other cinchona alkaloids.

CINCHONINE ($\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}$).

1. To a solution of the sulphate add NH_4OH ; a white precipitate results, *insoluble* in excess.

2. To a saturated solution add chlorine water and then NH_4OH in slight excess; a white precipitate is formed, free from green color.

ATROPINE ($\text{C}_{17}\text{H}_{22}\text{NO}_2$).

1. Add to a small quantity of the alkaloid a drop of H_2SO_4 , no change occurs; add to the mixture HNO_3 , no color is produced, showing the absence of and difference from morphine; similarly when a crystal of $\text{K}_2\text{Cr}_2\text{O}_7$ is added no change occurs, indicating the absence of and difference from strychnine.

2. To a small quantity of atropine in a test tube add H_2SO_4 and heat until it turns brown; dilute with water and boil, when the characteristic odor of orange flowers will be developed.

3. Boil with $\text{K}_2\text{Cr}_2\text{O}_7$ and dilute H_2SO_4 , and add KOH in excess, when a herring-like odor will be given off.

CAFFEINE ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$).

1. To an aqueous solution of the alkaloid add a solution of potassio-mercuric iodide; no precipitation occurs, indicating the absence of and distinction from most other alkaloids.

2. Treat a small quantity with chlorine water and evaporate to dryness, when a yellow mass will remain, which on moistening with NH_4OH will become purple.

VERATRINE.

1. To a small quantity on a crucible lid, add a drop of HNO_3 ; it dissolves with a yellow color, which soon passes to a reddish-yellow, then to an intense scarlet and, finally, to a violet-red.

2. Similarly, to another portion add H_2SO_4 ; very little change takes place, but on warming a resinous mass is formed, which dissolves with a deep red color.

3. Repeat the above reaction, using HCl , when a blood-red color results.

SALICIN ($\text{C}_{11}\text{H}_{10}\text{O}_7$).

1. Add cold, concentrated H_2SO_4 when a red color is produced, which disappears on adding water, a dark red powder insoluble in water and in alcohol being deposited.

2 The aqueous solution of salicin should not be precipitated by tannic or picric acids, nor potassio-mercuric iodide, indicating the absence of and difference from most alkaloids.

SANTONIN ($\text{C}_{15}\text{H}_{12}\text{O}_3$).

1. To an alcoholic solution of KOH add santonin; it will dissolve with a red color, gradually becoming colorless.

2. To another portion of santonin add cold concentrated H_2SO_4 ; there is gradually formed a yellow color, becoming red and, finally, brown.

3. Santonin should give no precipitates with the ordinary reagents for the alkaloids.

NOTE.—All the preceding organic compounds may be tested for mineral impurities by heating on platinum foil; no residue should be left.

PART THIRD.

QUANTITATIVE ANALYSIS.

PART III.—QUANTITATIVE CHEMICAL ANALYSIS.

SECTION I.

GRAVIMETRIC ESTIMATION.

PRELIMINARY DIRECTIONS.

The following course supposes the student to be familiar with the operations in *qualitative analysis*, as well as with the process of weighing, or in a position to be instructed by some one familiar with the use of analytical balances and weights. The following rules, however, should be kept constantly before those using a fine balance :—

1. *Never put any chemical substance directly on the pan of a balance, but always on a clean, dry watch crystal.*
2. *Never put on or take off a weight, or anything else, from a balance when it is resting on the knife edges.*
3. *All volatile acids and other corrosive substances should be weighed in stoppered weighing tubes.*
4. *Do not keep the balance open longer than is absolutely necessary.*

PRECIPITATION.

This should be conducted in beaker glasses. Avoid a large excess of the reagent, except in a few cases where it is directed. The filtrate should always be tested with a few drops more of the reagent, to determine that the precipitation has been complete. Distilled water is used in all quantitative determinations.

FILTRATION.

A filter paper having a very small ash should be used ; the Swedish is probably the best. Plain filters are always used, made by folding a circular piece of the paper twice, and opening so as to form a cone, which will fit exactly into a funnel, and allow all the liquid to pass through the precipitate and

escape at the lower point into the neck of the funnel. The precipitate should be allowed to settle in the beaker after precipitation; the clear supernatant liquid is then poured on the filter, using a glass rod against the edge of the beaker, to conduct it into the funnel without loss. The precipitate is then washed into the filter with the aid of the wash bottle, and the washing continued, until by the appropriate test it is found to be complete. The washing, in many cases, is to be done with hot water.

DRYING.

The filter and its contents are usually dried in the funnel when intended for ignition, but if to be weighed without burning, it is transferred to two watch crystals clamped together, and dried in an air bath, at from 120° to 130° C., until it ceases to lose weight.

IGNITION.

This is usually done in a platinum or porcelain crucible, the precipitate being separated as much as possible from the filter, and the latter burned on the lid, then placed in the crucible with the precipitate and the whole brought to a low or bright red heat, as the case requires. It is then cooled in a desiccator, until nearly the temperature of the balance room, when it is ready for weighing.

Examples for Practice by Gravimetric Estimation.

BARIUM CHLORIDE ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$).

Estimation of the Barium.

Weigh about .500 gram of the pure salt, dissolve in 100 c. c. of water in a beaker of about 200 c. c. capacity. Add dilute sulphuric acid, drop by drop, as long as any precipitate is produced, and then boil the mixture. Allow the precipitate to settle, pour the clear supernatant liquid into a filter, boil with a fresh quantity of water, and after pouring in the clear liquid, transfer the precipitate to the filter. Remove the small part of the precipitate which adheres to the sides of the beaker with a glass rod having a short section of rubber tubing slipped over the end. Wash the precipitate with hot water,

until the washings cease to cause a turbidity with solution of barium chloride, then dry, ignite and weigh as barium sulphate, BaSO_4 .

The following calculation will serve to illustrate the general method :—

$$\begin{array}{rcl} \text{Ba} & = & 136.8 = 56.16 \text{ per cent.} \\ \text{Cl}_2 & = & 70.8 = 29.06 \text{ " } \\ 2\text{H}_2\text{O} & = & 36. = 14.78 \text{ " } \\ \hline & & 243.6 \quad 100.00 \end{array}$$

Supposing we take .365 gram of barium chloride and find .349 gram of barium sulphate, we have as—

Molecular wt. of BaSO_4	:	Atomic wt. of Ba.	:	Wt. of BaSO_4 found.	:	Wt. of Ba found
232.8	:	136.8	:	.349	:	.205 +
Wt. of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ taken.	:	Wt. of Ba found	:		:	Per cent of Ba found.
As .365	:	.205 +	:	100	:	56.16

ESTIMATION OF THE CHLORINE.

To accomplish this weigh another portion of the salt, dissolve in about 100 c.c of water, acidify with HNO_3 , add AgNO_3 in slight excess and heat to the boiling point. Stir the mixture while hot, until the precipitate coagulates, allow to settle, decant the clear liquid to a filter, then rapidly transfer the precipitate, and wash it well with hot water, dry and transfer the precipitate to a crucible, burning the filter on the crucible lid. If an appreciable amount of the precipitate adheres to the filter it is best to moisten the residue after burning with a drop or two of nitrohydrochloric acid, to reconvert any metallic silver which may have formed into chloride. The lid, crucible and contents are heated in an air bath to 130° and weighed. The whole operation should be conducted as rapidly as possible, as silver chloride is acted on by the light.

COPPER SULPHATE ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

Estimation of the Copper.

Weigh from .500 to 1 gram, dissolve in a small quantity of water in a porcelain dish; add potassium hydrate in slight excess and boil, to convert the cupric hydrate first formed into

cupric oxide. Wash two or three times by decantation, then transfer to the filter and again wash with hot water until the filtrate ceases to change red litmus paper. The precipitate is separated from the filter, and the latter after burning is moistened with a drop of nitric acid and again heated, to reconvert any metallic copper which may have been formed; this residue is then transferred to the crucible with the precipitate and the whole ignited and weighed as cupric oxide CuO .

ESTIMATION OF SULPHURIC ACID.

Weigh another portion of the copper sulphate, dissolve and precipitate the sulphuric acid with barium chloride. Treat the precipitate exactly as in the estimation of barium.

POTASSIUM NITRATE (KNO_3).

Estimation of the Potassium.

To a weighed portion of the salt, dissolved in a small quantity of water, add hydrochloric acid, and evaporate to dryness, dissolve in a small quantity of water, add platinic chloride in excess and evaporate nearly to dryness on a water bath, keeping the water in the bath just below the boiling point. Add 80 per cent. alcohol to the residue, allow to stand some time, then transfer to a small weighed filter, and wash repeatedly with small quantities of the same strength alcohol. Dry the precipitate first in the air, then in the air bath at 130°C ., and weigh between two watch crystals. From the potassium platinic chloride (K_2PtCl_6) the potassium is readily calculated.

ESTIMATION OF THE NITRIC ACID.

Fuse in a platinum crucible, at a low temperature, some potassium nitrate, and pour out on a warm porcelain slab. Ignite two or three grams of silica in the crucible and mix with it about one-fourth its weight of the fused and powdered nitre. Bring the mixture to a low red heat and keep at that temperature until it ceases to lose weight. The loss indicates the amount of N_2O_5 from which the HNO_3 can be calculated. Sulphates and chlorides are not decomposed at this temperature.

MAGNESIUM SULPHATE ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

To a weighed quantity of the salt dissolved in water, add solution of ammonium chloride in slight excess, then water of ammonia until after stirring the mixture smells distinctly of it. If the ammonium hydrate produce a precipitate, it is evidence that sufficient ammonium chloride has not been added. When the solution remains clear after the addition of the hydrate, add sodium phosphate in excess, stir the mixture, without allowing the rod to touch the sides of the beaker, and set aside for twenty-four hours without warming.

The clear liquid is poured on a filter and the precipitate then transferred to the same, using a little of the clear filtrate to wash the last portions on if necessary.

The precipitate is then washed with a mixture of three parts water and one part ammonia water until a few drops of the washings acidified with nitric acid give no precipitate with silver nitrate.

The precipitate is then dried and transferred to a crucible, the filter burned separately and the whole ignited strongly until the weight is constant. The residue consists of magnesium pyrophosphate— $\text{Mg}_2\text{P}_2\text{O}_7$.

ESTIMATION OF THE SULPHURIC ACID.

The sulphuric acid is estimated in another portion of the salt by precipitation with barium chloride in the presence of hydrochloric acid. The resulting barium sulphate is collected, washed and ignited as under barium.

ESTIMATION OF THE WATER.

The water of crystallization may be estimated in magnesium sulphate by exposing a weighed quantity of the salt in a crucible to a low red heat until the weight becomes constant.

CALCIUM CARBONATE (CaCO_3).*Estimation of the Calcium.*

Dissolve a weighed quantity of the carbonate in dilute hydrochloric acid, avoiding excess of acid, add ammonium hydrate until slightly alkaline, then ammonium oxalate, and

set aside for twelve hours. Decant the clear supernatant liquid to a filter, wash once or twice by decantation, transfer the precipitate to the filter and wash with small portions of water, allowing each portion to completely run through before adding more. Dry and ignite the precipitate, using a strong Bunsen burner with a chimney, so as to bring the crucible to a white heat, until it ceases to lose weight; if this cannot be effected with a Bunsen burner, use a blast lamp. The residue is weighed as calcium oxide, CaO .

ESTIMATION OF THE CARBONIC ACID.

This in some cases is done by ignition, but the method adapted to all cases is to treat the carbonate with an acid, as HCl or H_2SO_4 , and estimate the loss of CO_2 . This is best accomplished by using a *carbonic acid apparatus*, that known as Schroetter's is probably the best.

An apparatus may be constructed, however, by taking a small, wide-mouth flask, and adapting to it a small tube containing calcium chloride. A weighed quantity of the material is then placed in the flask with some water, a test tube containing sulphuric acid is put in so as to retain the acid until the cork with the drying tube is fixed in place, and the whole apparatus weighed.

The flask is then turned over so as to allow some of the acid to flow out, and this is repeated, allowing only a small quantity to run out at a time, until the carbonate has been completely decomposed. The flask is then heated, to drive out all the CO_2 , and after cooling the apparatus is weighed. The loss indicates the amount of CO_2 in the material used.

FERROUS SULPHATE ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

Iron is usually estimated gravimetrically in the ferric state; for this purpose the above salt when pure will answer the purpose. For the estimation of ferrous iron see the next section.

A weighed quantity of the salt is dissolved in water, a few drops of sulphuric acid added and the mixture heated to the boiling point; nitric acid is then dropped in until oxidation

to ferric iron is effected, and then water of ammonia is added until the solution smells strongly of it after stirring. The precipitate of ferric hydrate is allowed to settle and the clear supernatant liquid poured on a filter, more water is added to the precipitate in the beaker and after pouring the clear liquid on the filter the precipitate is transferred to the same and washed thoroughly with hot water, until the washings cease to have an alkaline reaction. The precipitate is dried, ignited and weighed, the result being ferric oxide, Fe_2O_3 .

SECTION II.

VOLUMETRIC ESTIMATION.

Volumetric analysis is the process of determining the amount of a substance by the use of a suitable reagent in solution of a known strength. The requisite apparatus consists of a *liter flask* and a *1000 cubic centimeter cylinder*, in which to prepare the solutions. A *100 c. c. burette* (Geissler's is the most desirable) with a suitable holder. A few *pipettes*, assorted sizes, some of which are graduated to $\frac{1}{10}$ c. c. The simplest process is that by *neutralization*, where an alkali is determined by neutralizing it with standard solution of oxalic acid. In such a case it is necessary to have a means of knowing when the alkali is exactly neutralized. Such a substance is known as an *indicator*. Solution of litmus may be used, but a solution of phenolphthalein gives most satisfactory results; it is colorless in neutral or acid and bright red in alkaline solution. It is made by dissolving 1 part phenolphthalein in 25 parts alcohol and adding sufficient water to make 100 parts.

A *normal solution* contains in every liter the molecular weight of the compound in grams. This is sometimes made *semi-normal*, when the compound, an acid, for instance, is dibasic.

A *deci-normal* solution is one-tenth the strength of the normal one. While in some of the following examples the normal solution is used, that of deci-normal strength is recommended for the use of students.

VOLUMETRIC SOLUTION OF OXALIC ACID.



The semi-normal solution is used, containing 63 grams in 1 liter.

Take of oxalic acid, carefully purified by crystallization, 63 grams, transfer it to a liter flask, add about 800 c. c. of

water, agitate until dissolved and bring the measure, with water, to 1000 c. c.

ESTIMATION OF POTASSIUM HYDRATE.

Dissolve a convenient quantity of potassium hydrate, for instance .500 gram, in a beaker containing 100 c. c. of water; add three or four drops of the phenolphthalein solution; set the beaker on a piece of white paper and bring over it a burette containing some of the oxalic acid solution. Allow the acid solution to run in slowly, constantly stirring with a glass rod, until the red color just ceases to be visible. The proof of this is that one drop of a similar alkali solution will restore the red color. If the potassium hydrate were pure, it would be found that 8.94 c. c. were used, but if we suppose that 8.50 c. c. were necessary, we have every c. c. of the oxalic solution = .056 gram of KOH, therefore $8.50 \times .056 = .476$ gram—the amount of KOH in the .500 gram = 95.20 per cent.

One c. c. containing 0.063 gram of oxalic acid is the equivalent of—

	GRAM.
Ammonia, NH_3 ,	0.0170
Ammonium Carbonate, $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{NH}_2\text{CO}_2$,	0.0523
Potassium Acetate, $\text{KC}_2\text{H}_3\text{O}_2$ (after ignition),	0.0980
Potassium Bicarbonate, KHCO_3 ,	0.1000
Potassium Carbonate (dry), K_2CO_3 ,	0.0690
Potassium Citrate, $\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ (after ignition),	0.1080
Potassium Hydrate, KOH ,	0.0560
Potassium Permanganate, $\text{K}_2\text{Mn}_2\text{O}_8$,	0.0314
Potassium Sodium Tartrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (after ignition),	0.1410
Potassium Tartrate, $(\text{K}_2\text{C}_4\text{H}_4\text{O}_6) \cdot \text{H}_2\text{O}$ (after ignition),	0.1175
Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$,	0.1892
Lead Subacetate, $\text{Pb}_2\text{O}(\text{C}_2\text{H}_3\text{O}_3)_3$,	0.1367
Sodium Bicarbonate, NaHCO_3 ,	0.0840
Sodium Borate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$,	0.1910
Sodium Carbonate, crystallized, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$,	0.1430
Sodium Carbonate, anhydrous, Na_2CO_3 ,	0.0530
Sodium Hydrate, NaOH ,	0.0400

When carbonates are estimated it is necessary to boil, toward the end of the reaction, after each addition of the acid, in order to drive off the CO_2 , which affects the indicator.

VOLUMETRIC SOLUTION OF SODIUM HYDRATE. ($\text{NaOH} = 40$).

The normal solution is used, containing 40 grams in 1 liter.

As sodium hydrate is never, or very rarely absolutely pure, it is necessary to standardize this solution. For this take something more than the theoretical amount (about 50 grams) and dissolve in a liter of water. Place 100 c. c. of the standard oxalic acid solution in a beaker, and, having added the indicator, bring it under a burette containing some of the soda solution, and note the number of c. c. necessary to exactly neutralize the acid solution. Take of the alkaline solution ten times the number of c. c. necessary to neutralize the 100 c. c. of the acid solution, and add sufficient water to bring the measure to 1000 c. c. For instance, if it required 95 c. c. of the alkaline solution to neutralize the 100 c. c. of the oxalic acid solution, then $95 \text{ c. c.} \times 10 = 950 \text{ c. c.}$, which amount diluted to 1000 c. c. would make it exactly equal in strength to the oxalic solution.

One c. c. containing 0.040 of sodium hydrate NaOH , is the equivalent of—

	GRAM
Acetic Acid, absolute, $\text{HC}_2\text{H}_3\text{O}_2$,	0.0600
Citric Acid, crystallized, $\text{H}_3\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$,	0.0700
Hydrobromic Acid, absolute, HBr ,	0.0808
Hydrochloric Acid, absolute, HCl ,	0.0364
Hydriodic Acid, absolute, HI ,	0.1276
Lactic Acid, absolute, $\text{HC}_3\text{H}_5\text{O}_3$,	0.0900
Nitric acid, absolute, HNO_3 ,	0.0630
Oxalic Acid, crystallized, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$,	0.0630
Sulphuric Acid, absolute, H_2SO_4 ,	0.0490
Tartaric Acid, crystallized, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$,	0.0750

VOLUMETRIC SOLUTION OF POTASSIUM BICHROMATE ($\text{K}_2\text{Cr}_2\text{O}_7 = 294.8$).

A viginti-normal solution is used, containing 14.74 grams to 1 liter.

Place the necessary amount of the salt (14.74 grams) in a liter flask, add about 800 c. c. of water, agitate until dissolved, and bring the measure with water to 1000 c. c. This solution, when acidified with H_2SO_4 , is used in the estimation of iron in

the ferrous condition. The end of the reaction is determined by taking out a drop of the iron solution, and testing on a white porcelain surface with a drop of potassium ferricyanide solution; when this ceases to give a blue color the reaction is at an end.

One c. c. containing 0.01474 gram of potassium bichromate, $K_2Cr_2O_7$, is the equivalent of—

	GRAM.
Iron in ferrous condition, Fe,	0.01677
Ferrous Carbonate, $FeCO_3$,	0.03477
Ferrous Sulphate, $FeSO_4 \cdot 7H_2O$,	0.08337
Ferrous Sulphate (dry), $FeSO_4 \cdot H_2O$,	0.05097

VOLUMETRIC SOLUTION OF IODINE ($I = 126.6$).

A deci-normal solution is used, containing 12.66 grams in 1 liter.

Weigh the necessary amount of iodine (12.66 grams) in a stoppered tube, to prevent loss, as well as the corrosive action of the fumes on the balance. Also weigh 18 grams of potassium iodide and place in a liter flask with the iodine. Add about 100 c. c. of water. The iodine dissolves more readily in this strength of potassium iodide solution, besides it admits of more thorough agitation. When the solution is complete add water until the liquid measures 1000 c. c. Starch solution is used as an indicator in the determinations with the iodine solution.

One c. c. containing 0.01266 iodine is the equivalent of—

	GRAM
Arsenious Oxide, As_2O_3 ,	0.00494
Potassium Sulphite, crystallized, $K_2SO_3 \cdot 2H_2O$,	0.0097
Sodium Bisulphite, $NaHSO_3$,	0.0052
Sodium Hyposulphite, crystallized, $Na_2S_2O_3 \cdot 5H_2O$,	0.0248
Sodium Sulphite, crystallized, $Na_2SO_3 \cdot 7H_2O$,	0.0126
Sulphurous Oxide, SO_2 ,	0.0032

VOLUMETRIC SOLUTION OF SODIUM HYPOSULPHITE ($Na_2S_2O_3 \cdot 5H_2O = 248$).

A deci-normal solution is used, containing 24.8 grams in 1 liter.

Sodium hyposulphite cannot be prepared sufficiently pure to be relied on, consequently this solution must be standardized, therefore more than the theoretical amount is taken.

The U. S. Pharmacopœia recommends 32 grams. Dissolve this amount in 1000 c. c. of water; place 100 c. c. of the standard solution of iodine in a beaker and run in the hyposulphite solution until the color of iodine nearly disappears, then add a small quantity of starch solution and continue until the blue color is discharged. Multiply the number of cubic centimeters of the hyposulphite solution used by 10, and to that amount add sufficient water to bring the measure to 1000 c. c. The substances estimated by this solution either contain free iodine, or develop it on the addition of potassium iodide, so that starch solution may be used as an indicator.

One c. c. containing 0.0248 gram of sodium hyposulphite is the equivalent of—

	GRAM.
Bromine, Br,	0.00798
Chlorine, Cl,	0.00354
Iodine, I,	0.01266

VOLUMETRIC SOLUTION OF SILVER NITRATE

($\text{AgNO}_3 = 169.7$).

A deci-normal solution is used, containing 16.97 grams in 1 liter.

As silver nitrate can be obtained or prepared perfectly pure, the necessary amount (16.97 grams) is dissolved in sufficient distilled water to make 1000 c. c.

In testing one of the following compounds, ammonium chloride for instance, a weighed amount is taken, dissolved in water, and a few drops of potassium bichromate solution added. The silver nitrate solution is then run in until a red precipitate remains permanently. The silver combines with the chlorine until the latter is all used, when it forms with the chromic acid red silver chromate, so that its formation indicates the end of the reaction.

One c. c. containing 0.01697 gram of silver nitrate is the equivalent of—

	GRAM.
Ammonium Bromide, NH_4Br ,	0.00978
Ammonium Chloride, NH_4Cl ,	0.00534
Ferrous Bromide, FeBr_2 ,	0.01077
Ferrous Iodide, FeI_2 ,	0.01545
Hydrocyanic Acid, absolute HCN ,	0.00270

VOLUMETRIC ESTIMATION.

	GRAM.
Hydriodic Acid, HI,	0.01276
Potassium Bromide, KBr,	0.01188
Potassium Chloride, KCl,	0.00744
Potassium Cyanide, KCN,	0.01300
Potassium Iodide, KI,	0.01656
Sodium Bromide, NaBr,	0.01028
Sodium Chloride, NaCl,	0.00584

TABLE OF ELEMENTS.

ELEMENTS	SYMBOLS.	ATOMIC WEIGHT
Aluminium	Al	27
Antimony	Sb	120
Arsenic	As	74.9
Barium	Ba	136.8
Beryllium	Be	9.1
Bismuth	Bi	207.5
Boron	B	11
Bromine	Br	79.8
Cadmium	Cd	111.8
Cæsium	Cs	132.6
Calcium	Ca	40
Carbon	C	12
Cerium	Ce	140.2
Chlorine	Cl	35.4
Chromium	Cr	52
Cobalt	Co	58.9
Copper	Cu	63.2
Didymium	Dy	147
Erbium	Er	165.9
Fluorine	F	19
Gallium	G	68.8
Germanium	Ge	72.3
Gold	Au	196.2
Hydrogen	H	1
Indium	In	113.4
Iodine	I	126.6
Iridium	Ir	192.7
Iron	Fe	55.9
Lanthanum	La	138.5
Lead	Pb	206.5
Lithium	Li	7
Magnesium	Mg	24
Manganese	Mn	54
Mercury	Hg	199.7
Molybdenum	Mo	95.5
Nickel	Ni	58
Niobium	Nb	94

TABLE OF ELEMENTS.—*Continued.*

ELEMENTS.	SYMBOLS	ATOMIC WEIGHTS.
Nitrogen	N	14
Norwegium	Ng	214
Osmium	Os	198.5
Oxygen	O	16
Palladium	Pd	105.7
Phosphorus	P	31
Platinum	Pt	194
Potassium	K	39
Rhodium	Rh	104.2
Rubidium	Rb	85.3
Ruthenium	Ru	104.2
Samarium	Sm	150
Scandium	Sc	44
Selenium	Se	78.8
Silicon	Si	28.2
Silver	Ag	107.7
Sodium	Na	23
Strontium	Sr	87.4
Sulphur	S	32
Tantalum	Ta	182.1
Tellurium	Te	128
Thallium	Tl	203.7
Thorium	Th	233.4
Tin	Sn	117.7
Titanium	Ti	48
Tungsten	W	183.6
Uranium	U	238.5
Vanadium	V	51.3
Ytterbium	Yb	172.7
Yttrium	Y	89.8
Zinc	Zn	64.9
Zirconium	Zr	84.4

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